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KNOCK-LIMITED PERFORMANCE OF BLENDS OF AN-F-28 FUEL CONTAINING 2 PERCENT AROMATIC AMINES - IV

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NACA

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

MEMORANDUM REPORT

for the

Army Air Forces, Air Technical Service Command

KNOCK-LIMITED PERFORMANCE OF BLENDS OF AN-F-28 FUEL CONTAINING 2 PERCENT AROMATIC AMINES - IV

By Henry E. Alquist and Leonard K. Tower

SUMMARY

Tests were conducted to investigate the effect of 2-percent additions of 13 aromatic amines on the knock-limited performance of 28-R fuel in a CFR engine. Knock tests of 28-R fuel and of 13 aromatic amines blended with 28-R fuel in 2-percent concentrations were conducted with a modified F-4 engine at three sets of operating conditions. The amines were synthesized or purchased and purified at the Cleveland laboratory of the NACA and included the following: N-methylcumidines, N-methylxylidines, p-ethylaniline, o-cumidine, o-ethylaniline, N,N-dimethyl-2,4,6-trimethylaniline, N,N-dimethyl-2-methyl-5-isopropylaniline, N-methyltoluidines (80 percent p-, 20 percent o-), N-methyltoluidines (60 percent p-, 40 percent o-), N-propylaniline, N-tert-butylaniline, 2,5-xylidine, and N-methyl-p-tert-butylaniline. Ratings were also determined for 28-R and all the test blends with an F-3 engine.

The results of knock-limited performance tests with the modified F-4 engine to determine the antiknock effectiveness of 2-percent blends of 13 aromatic amines are summarized as follows:

1. The following aromatic amines were effective antiknock additives when tested at moderate engine conditions over the complete fuel-air ratio range:

N-Methylcumidines
N-Methylxylidines
p-Ethylaniline
N-Methyltoluidines (80 percent p-, 20 percent o-)
N-Methyltoluidines (60 percent p-, 40 percent o-)
2,5-Xylidine
N-Methyl-p-tert-butylaniline

These amines gave good rich-mixture response at standard F-4 operating conditions but were sensitive to engine severity at lean fuel-air ratios.

INTRODUCTION

A general investigation on the effectiveness of aromatic amines as antiknock additives for aviation fuels is being conducted at the Cleveland laboratory of the NACA at the request of the Army Air Forces, Air Technical Service Command. This report is part IV of a series of five reports presenting knock data on a total of 48 aromatic amines. (See references 1 to 3.) The low-temperature solubility of the amines and the suitability for overwater storage of their gasoline blends are presented in references 4 to 6. The present paper reports knock-limited performance data, obtained during August and September 1944, for 13 aromatic amines. It is emphasized that knock in a CFR engine is the sole criterion for evaluating the amines in this report.

APPARATUS AND TEST PROCEDURE

The aromatic amines tested were prepared by the Organic Synthesis Section of the Cleveland laboratory under the direction of Dr. W. T. Olson. The amines were distilled through a fractionating column, and a narrow fraction (approximately 1° C) in the middle of the boiling range was selected for the engine tests.

Knock-limited data were obtained with the same modified F-4 engine, base stock, and operating conditions as reported in references 2 and 3. The three sets of operating conditions, ranging from severe to mild, were as follows:

	Inlet-air temperature (°F)	Spark advance (deg B.T.C.)	Coolant temperature (°F)
F-4 method	225	45	375
Modification A	250	30	250
Modification B	150	30	250

At each of these sets of conditions, 28-R and a blend of 28-R containing 2 percent of an aromatic amine were tested on the same day.

F-3 ratings for 28-R and all the fuel blends were also obtained.

DISCUSSION OF RESULTS

Figures 1 to 13 present the knock-limited performance data for the 13 aromatic amines tested under three sets of conditions. Each figure compares the effects of the transition from severe to mild engine conditions for 28-R fuel and a 2-percent addition of each aromatic amine to this fuel. Table I lists the amines tested and summarizes the relative power obtained by their addition to 28-R fuel when tested under supercharged conditions. Table II presents the F-3 ratings of 28-R fuel with and without the addition of the aromatic amines.

When the engine was operated according to F-4 specifications, none of the amines consistently increased the knock-limited power above that of 28-R fuel at lean mixtures, as shown in table I; however, the N-methylcumidines, N-methylxylidines, p-ethylaniline, both the N-methyltoluidines, 2,5-xylidine, and the N-methyl-p-tert-butylaniline exhibited desirable rich-mixture characteristics. When tested under the modified conditions, these amines acted as good antiknock additives over the complete range of fuel-air ratios. The F-3 ratings presented in table II show an improvement in the performance of 28-R fuel by the addition of each of the aforementioned amines except 2,5-xylidine and N-methyl-p-tert-butylaniline.

Among the 13 aromatic amines considered herein, o-cumidine, o-ethylaniline, N,N-dimethyl-2,4,6-trimethylaniline, N,N-dimethyl-2-methyl-5-isopropylaniline, and N-tert-butylaniline showed no beneficial characteristics as antiknock agents. On the average, N-propylaniline promoted knock under F-4 conditions, but improvements up to 6 percent were observed over the fuel-air-ratio range tested at the modified conditions. (See fig. 10(a).)

Aromatic-amine compounds having alkyl radicals substituted in the ortho position appeared to be less satisfactory antiknock agents than those with substitutions in the meta or para positions. This finding is illustrated by comparing o-ethylaniline with p-ethylaniline (figs. 3 and 5) and N-methyltoluidines (80 percent p-, 20 percent o-) with N-methyltoluidines (60 percent p-, 40 percent o-) (figs. 8 and 9). Table III presents a comparison of the relative powers afforded by various aromatic amines having ortho-substituted radicals with the powers obtained with amines having para-substituted radicals.

Adding 2 percent of 2,5-xylidine to 28-R fuel gave much the same result as that previously obtained with 2,4-xylidine, 2,6-xylidine, and commercial xylidines. (See fig. 12 and references 1 and 3.) At

moderate engine conditions 2,5-xylidine acted as a good antiknock additive but, when the severity of engine conditions was increased, the power improvement became increasingly dependent on fuel-air ratio.

Comparison of the data for N-methylxylidines reported herein (fig. 2) with the data for commercial xylidines in reference 1 indicates that little choice can be made between them. The small difference at certain fuel-air ratios between their respective relative knock-limited powers is considered insignificant.

Slight differences between the indicated specific fuel consumptions of 28-R fuel and those of blends containing an aromatic amine were not considered significant.

SUMMARY OF RESULTS

The results of knock-limited performance tests with the modified F-4 engine to determine the antiknock effectiveness of 2-percent blends of 13 aromatic amines are summarized as follows:

1. The following aromatic amines were effective antiknock additives when tested at moderate engine conditions over the complete fuel-air-ratio range:

N-Methylcumidines
N-Methylxylidines
p-Ethylaniline
N-Methyltoluidines (80 percent p-, 20 percent o-)
N-Methyltoluidines (60 percent p-, 40 percent o-)
2,5-Xylidine
N-Methyl-p-tert-butylaniline

These amines gave good rich-mixture response at F-4 conditions but were sensitive to engine severity at lean fuel-air ratios.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, December 21, 1944.

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4. Olson, Walter T., and Kelly, Richard L.: The Low-Temperature Solubility of Aniline, the Toluidines, and Some of Their N-Alkyl Derivatives in Aviation Gasoline. NACA Memo. rep., June 5, 1944.

5. Olson, Walter T., Tischler, Adelbert O., and Goodman, Irving A.: Gasoline-Water Distribution Coefficients of 27 Aromatic Amines. NACA Memo. rep., Aug. 3, 1944.

6. Kelly, Richard L.: The Low-Temperature Solubility of 24 Aromatic Amines in Aviation Gasoline. NACA MR No. E4K17, Nov. 17, 1944.

TABLE I - SUMMARY OF ANTIKNOCK EFFECTIVENESS OF AROMATIC-AMINE ADDITIONS TO 28-R FUEL

	Inlet-air temperature (°F)	Coolant temperature (°F)	Spark advance (deg B.T.C.)
F-4 method	225	375	45
Modification A	250	250	30
Modification B	150	250	30

Aromatic amine (2-percent addition to 28-R)	Relative power = $\frac{imep(\text{aromatic amine plus 28-R})}{imep(28\text{-R})}$											
	F/A = 0.062			F/A = 0.070			F/A = 0.090			F/A = 0.110		
	F-4 method	Modification A	Modification B	F-4 method	Modification A	Modification B	F-4 method	Modification A	Modification B	F-4 method	Modification A	Modification B
28-R	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
N-Methylcumidines	.99	1.17	1.14	.98	1.11	1.16	1.08	1.15	1.14	1.13	1.16	1.14
N-Methylxylidines	1.00	1.01	1.13	1.03	1.05	1.13	1.00	1.09	1.11	1.08	1.11	1.11
p-Ethylaniline	.97	1.10	1.12	.97	1.13	1.12	1.04	1.12	1.14	1.09	1.13	1.12
o-Cumidine	.92	.99	1.00	.93	.98	1.03	.90	1.01	1.06	.97	1.01	1.05
o-Ethylaniline	1.00	1.01	1.04	1.00	1.03	1.01	.92	1.05	1.04	1.00	1.04	1.07
N,N-Dimethyl-2,4,6-trimethylaniline	.97	1.04	.98	.95	.98	.98	.88	.96	.97	.94	.97	.98
N,N-Dimethyl-2-methyl-5-isopropylaniline	.97	.97	1.01	.95	.97	.98	.94	.98	.99	.97	.99	1.00
N-Methyltoluidines (80% p-, 20% o-)	.98	1.14	1.16	.95	1.18	1.15	1.04	1.15	1.16	1.14	1.14	1.09
N-Methyltoluidines (60% p-, 40% o-)	1.01	1.05	1.10	1.00	1.12	1.14	1.01	1.15	1.13	1.13	1.13	1.11
N-Propylaniline	1.03	1.00	1.03	.98	1.06	1.06	.96	1.03	1.04	1.02	1.02	1.06
N-tert-Butylaniline	.97	1.02	1.01	.84	1.00	1.01	.97	1.00	1.01	1.02	.99	1.02
2,5-Xylidine	.98	1.01	1.12	.81	1.07	1.12	.97	1.10	1.09	1.10	1.07	1.11
N-Methyl-p-tert-butylaniline	1.00	1.11	1.12	.91	1.13	1.14	1.02	1.16	1.10	1.14	1.12	1.10

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TABLE II - F-3 RATINGS OF 2-PERCENT BLENDS OF AROMATIC AMINES AND 28-R FUEL

Aromatic amine (2-percent addition to 28-R fuel)	F-3 rating	
	Tetraethyl lead in S-3 reference fuel, ml/gal, or octane number	Performance number
28-R	100	100
N-Methylcumidines	0.04	101
N-Methylxylidines	0.06	102
p-Ethylaniline	0.04	101
o-Cumidine	100	100
o-Ethylaniline	100	100
N,N-Dimethyl-2,4,6-trimethylaniline	98	93
N,N-Dimethyl-2-methyl-5-isopropylaniline	98.8	96
N-Methyltoluidines (80% p-, 20% o-)	0.04	101
N-Methyltoluidines (60% p-, 40% o-)	0.03	101
N-Propylaniline	100	100
N-tert-Butylaniline	100	100
2,5-Xylidine	100	100
N-Methyl-p-tert-butylaniline	100	100

TABLE III

COMPARISON OF RELATIVE KNOCK-LIMITED POWERS OF AMINES WITH ORTHO- AND PARA-SUBSTITUTED RADICALS

[Operating condition, modification A: inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.]

Aromatic amine	Relative power = $\frac{imep_{(amine + 28\text{-}R)}}{imep_{(28\text{-}R)}}$	
	F/A = 0.062	F/A = 0.090
o-Toluidine[1]	1.03	1.08
p-Toluidine[1]	1.08	1.13
N-Methyl-p-toluidine[2]	1.13	1.20
N-Methyltoluidines (80% p-, 20% o-)	1.14	1.15
N-Methyltoluidines (60% p-, 40% o-)	1.05	1.15
p-Ethylaniline	1.10	1.12
o-Ethylaniline	1.01	1.05

[1]Data from reference 2.
[2]Data from reference 1.

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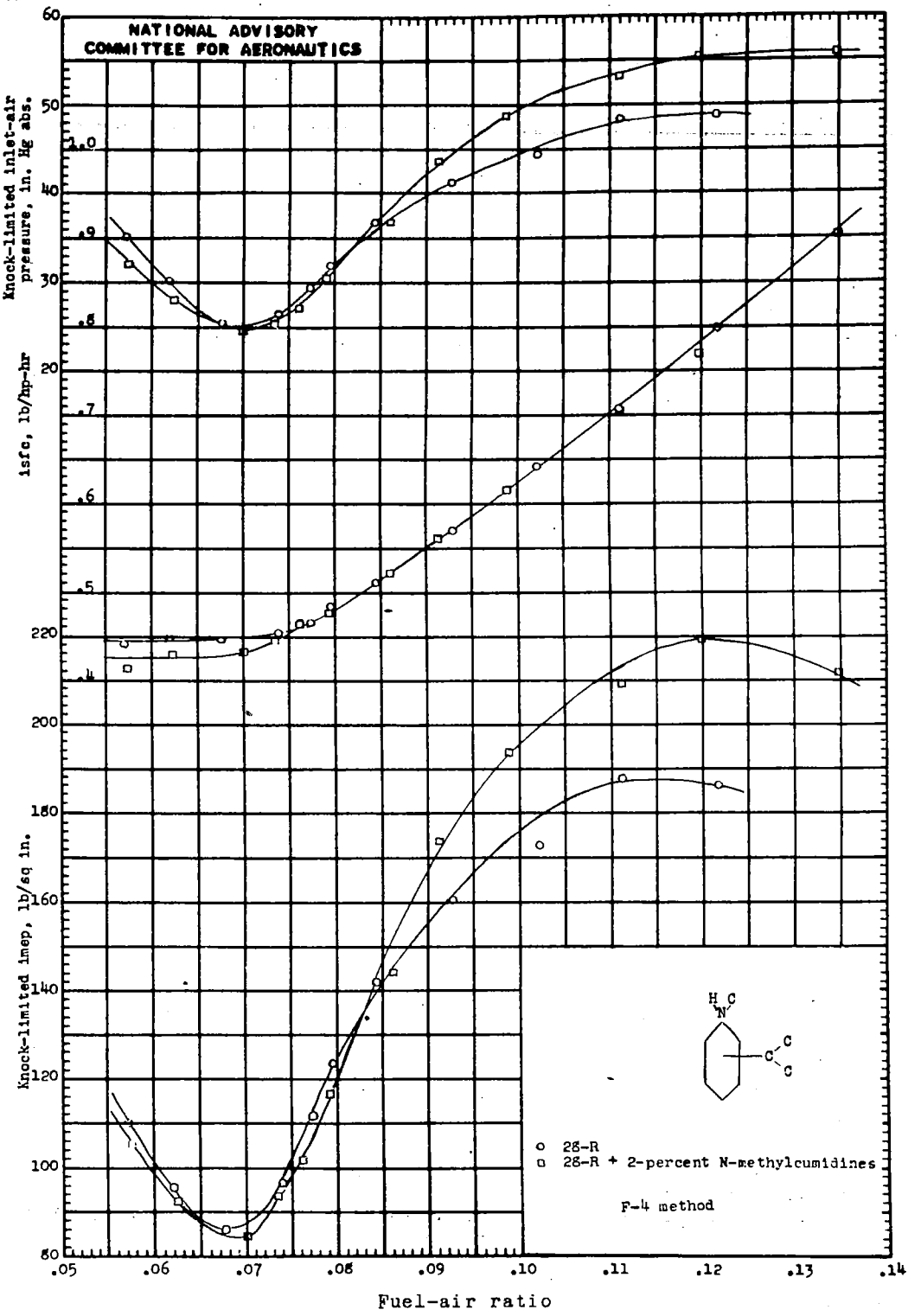
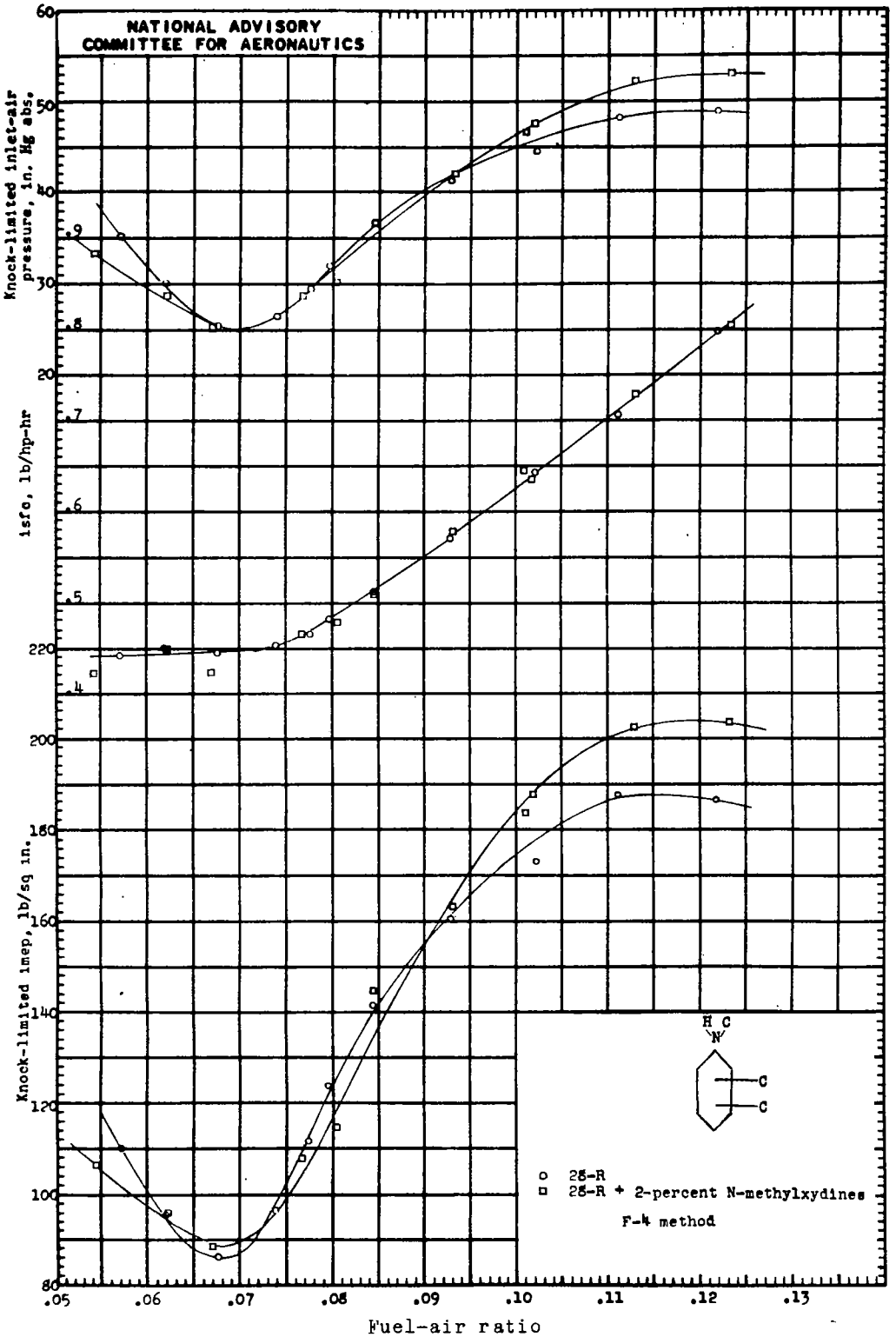


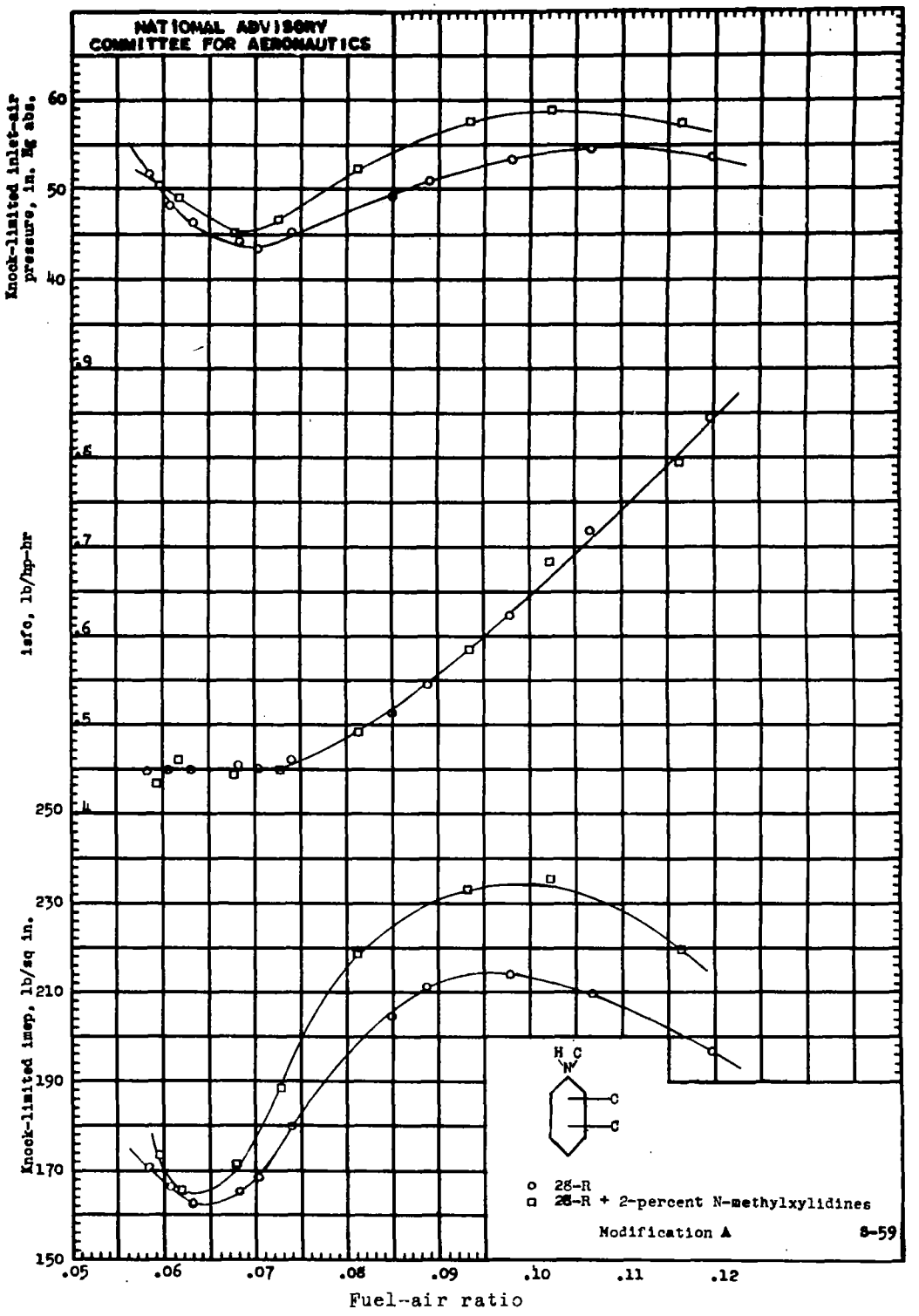
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 1. - Effect of addition of 2-percent N-methylcumidines to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



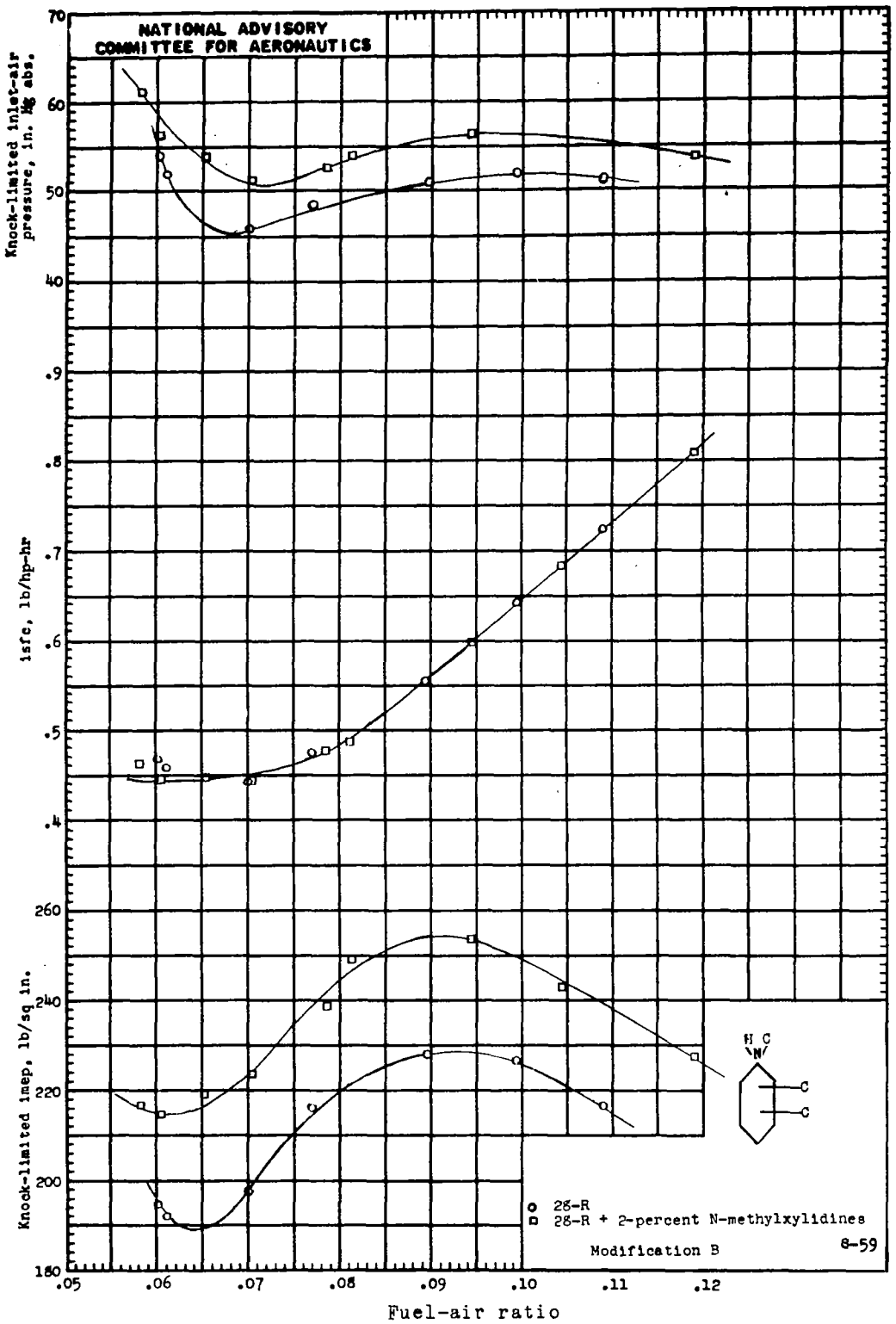
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 2. - Effect of addition of 2-percent N-methylxylidines to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



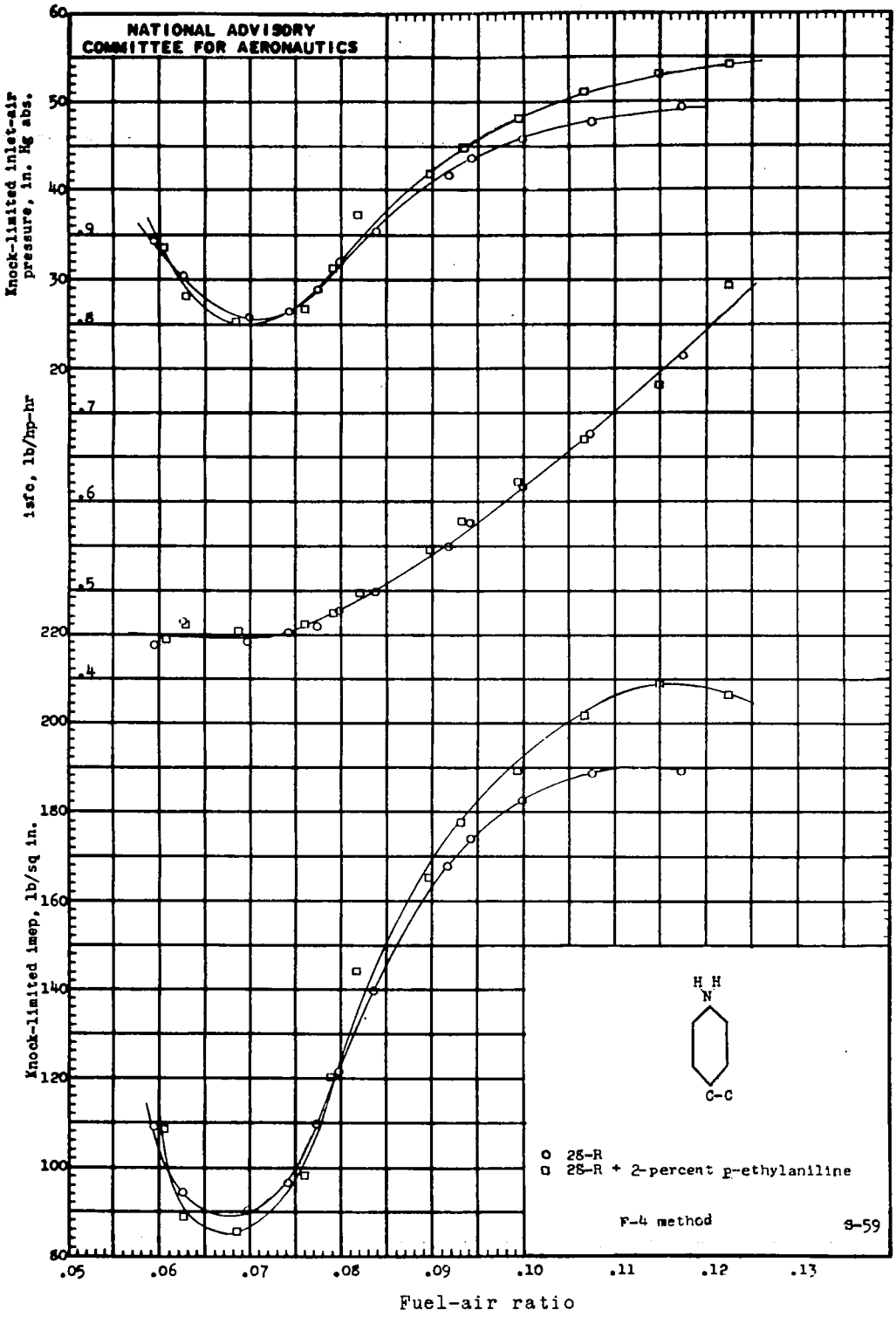
(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 2. - Continued. Effect of addition of 2-percent N-methylxylidines to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



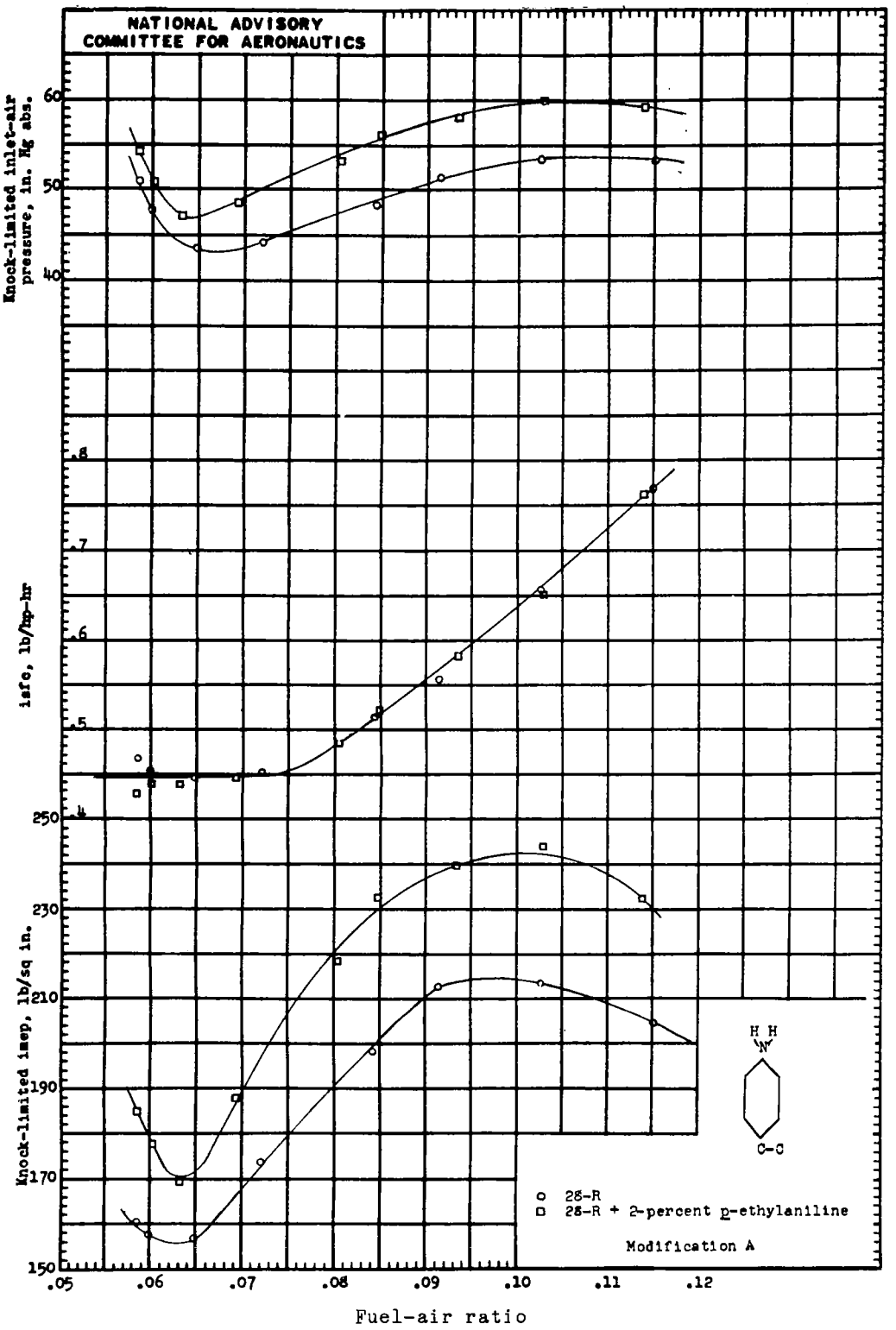
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 2. - Concluded. Effect of addition of 2-percent N-methylxylidines to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



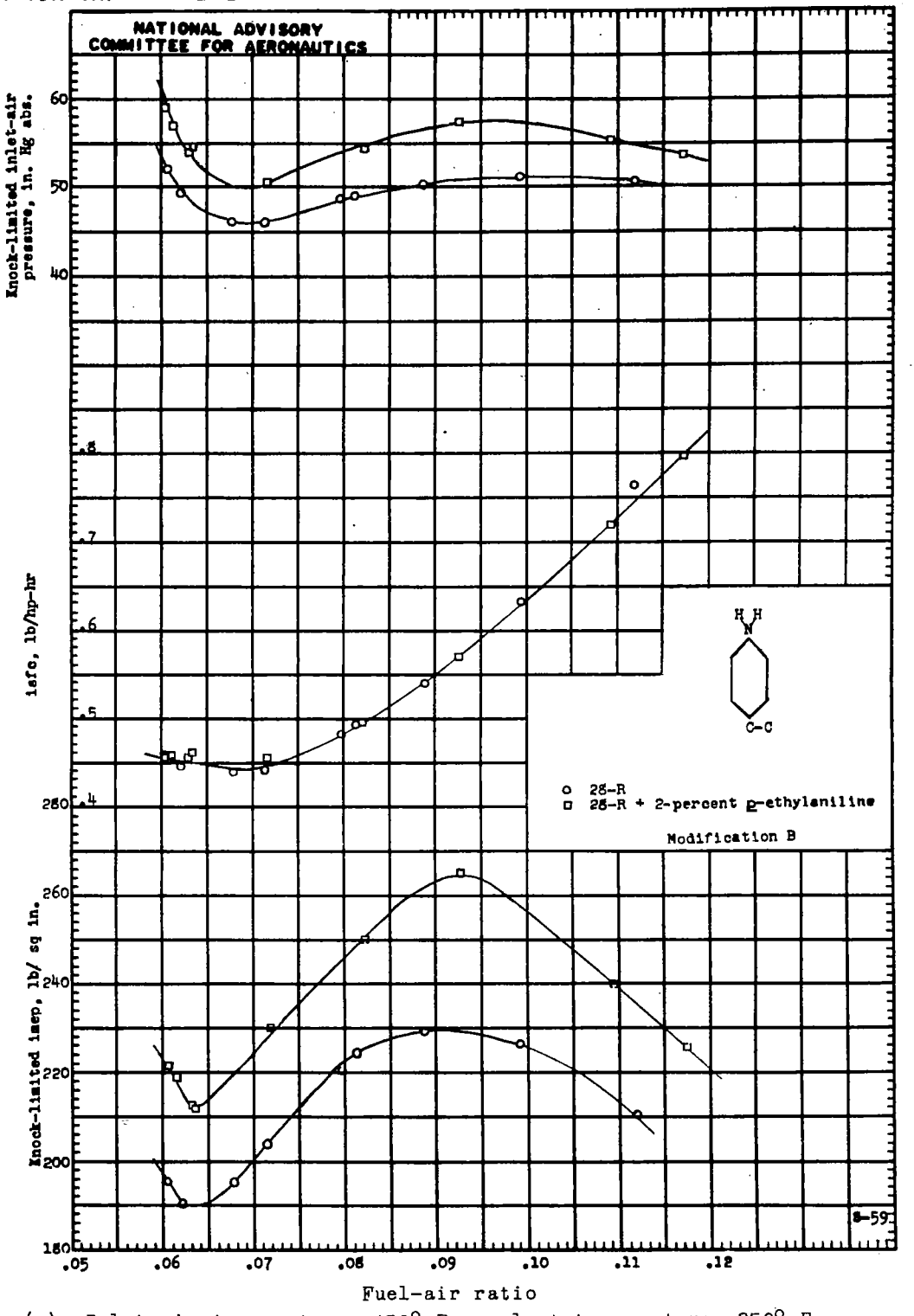
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 3. - Effect of addition of 2-percent p-ethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



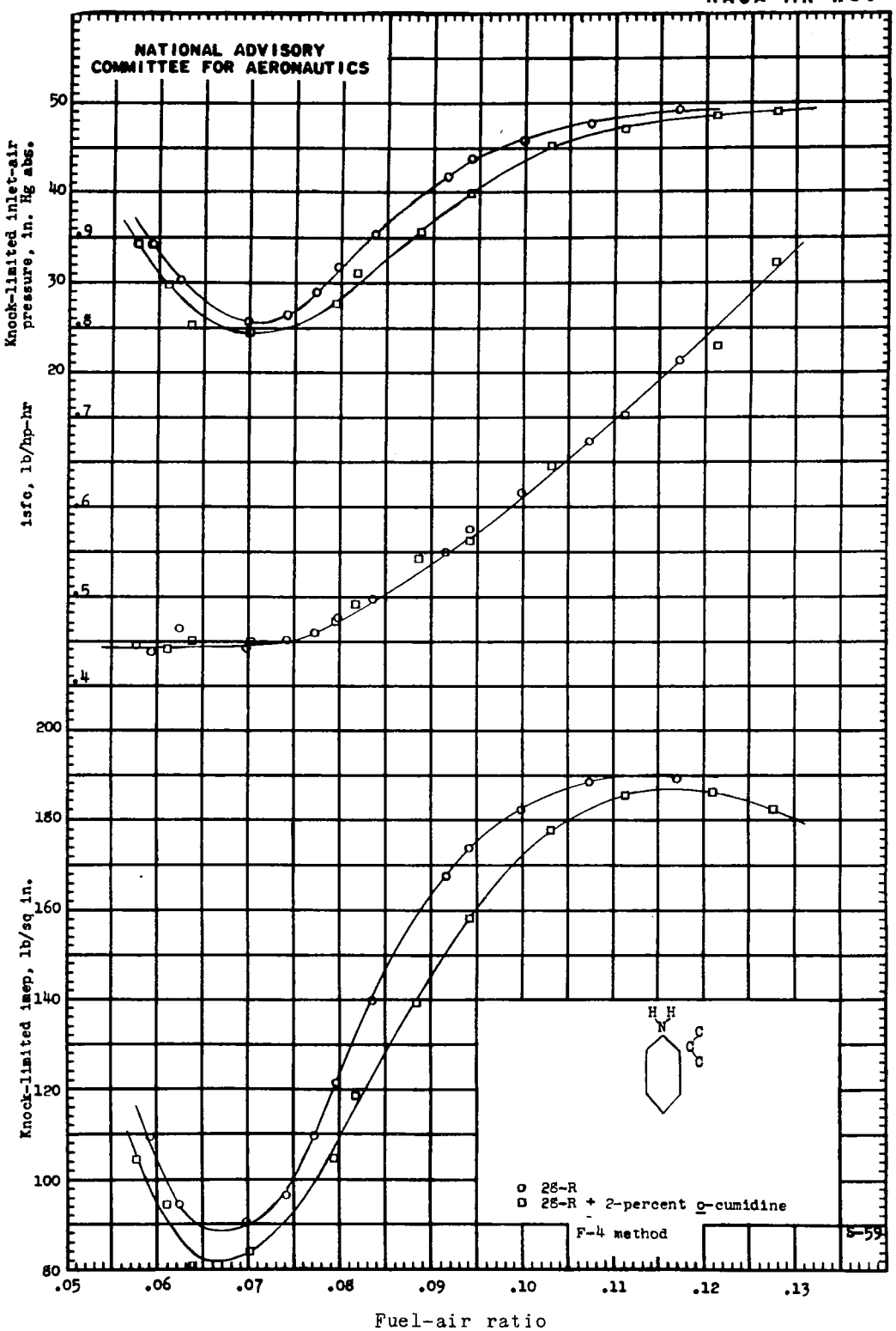
(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 3. - Continued. Effect of addition of 2-percent p-ethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



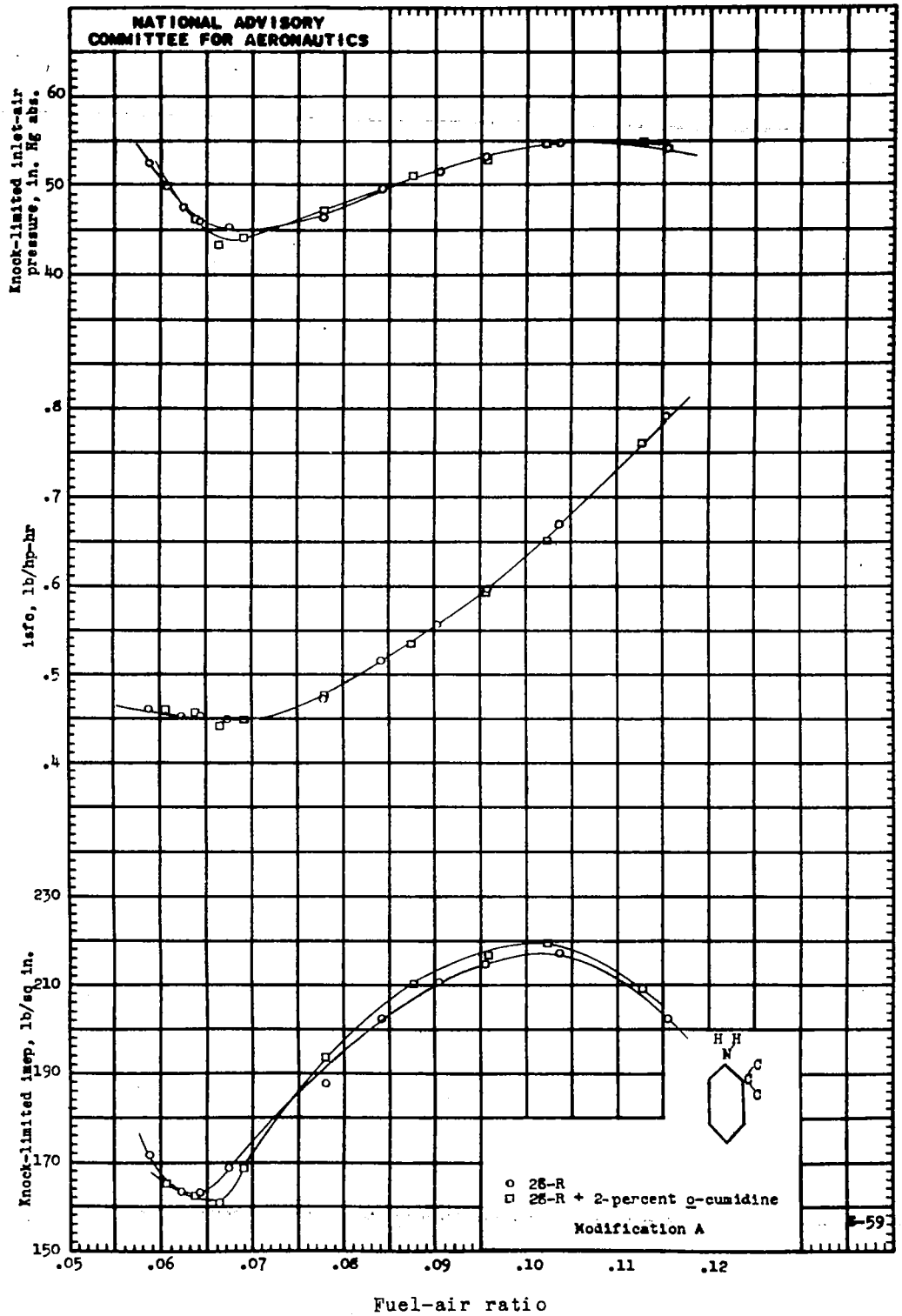
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 3. - Concluded. Effect of addition of 2-percent p-ethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



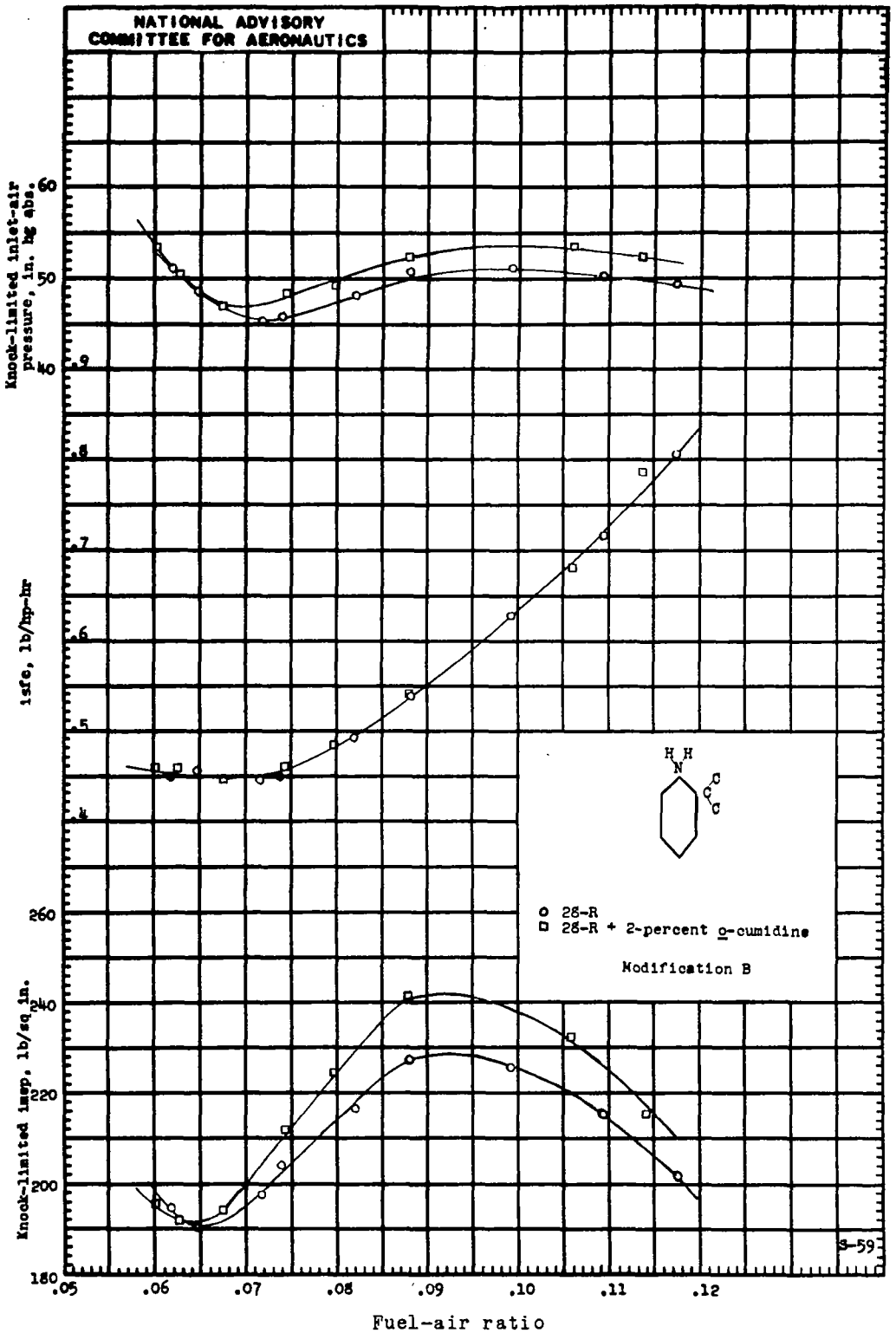
(a) Inlet-air temperature, 225° F; coolant temperature 375° F; spark advance. 45° B.T.C.

Figure 4. - Effect of addition of 2-percent o-cumidine to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



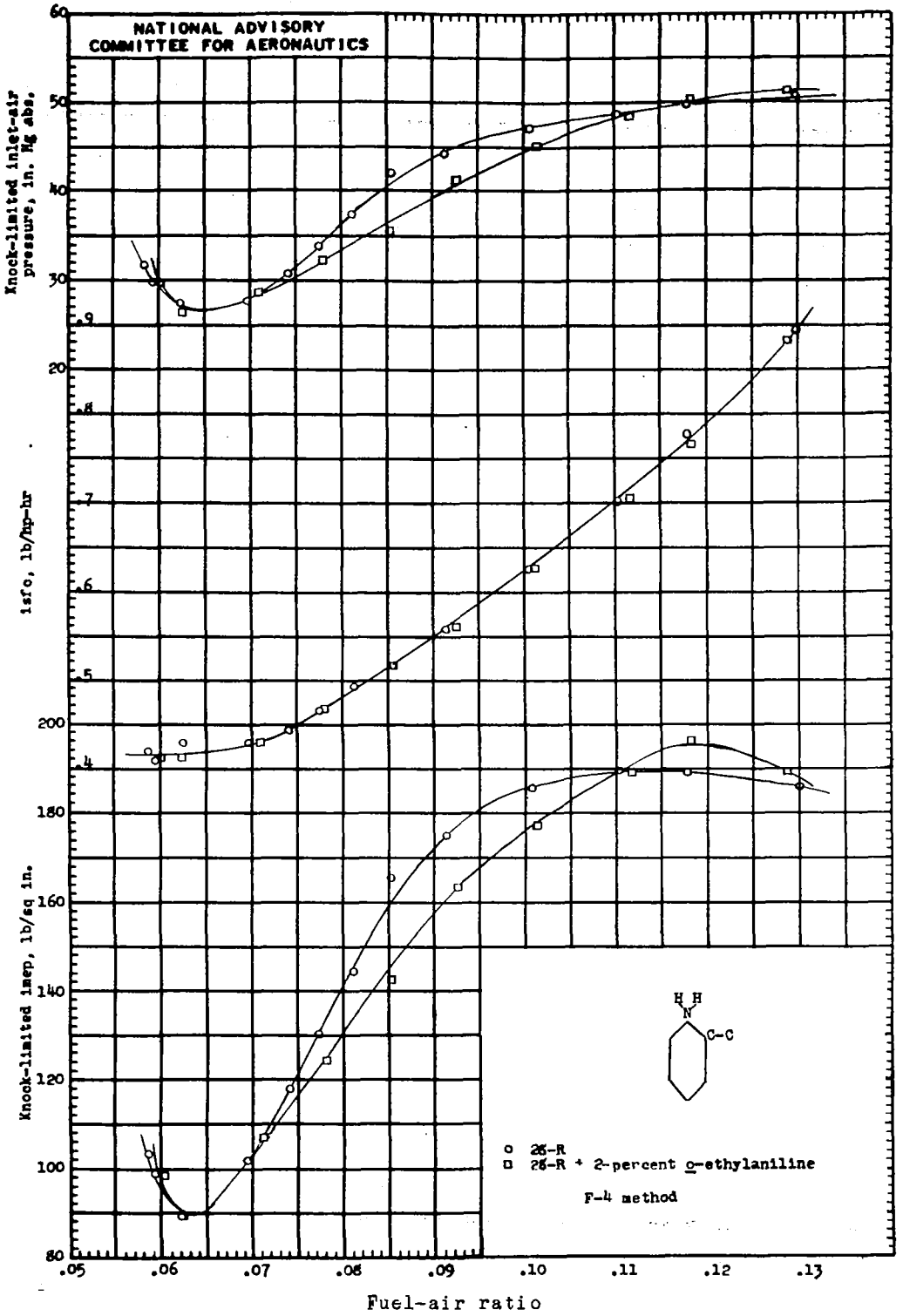
(b) Inlet-air temperature, 250° F; coolant temperature 250° F; spark advance, 30° B.T.C.

Figure 4. - Continued. Effect of addition of 2-percent o-cumidine to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



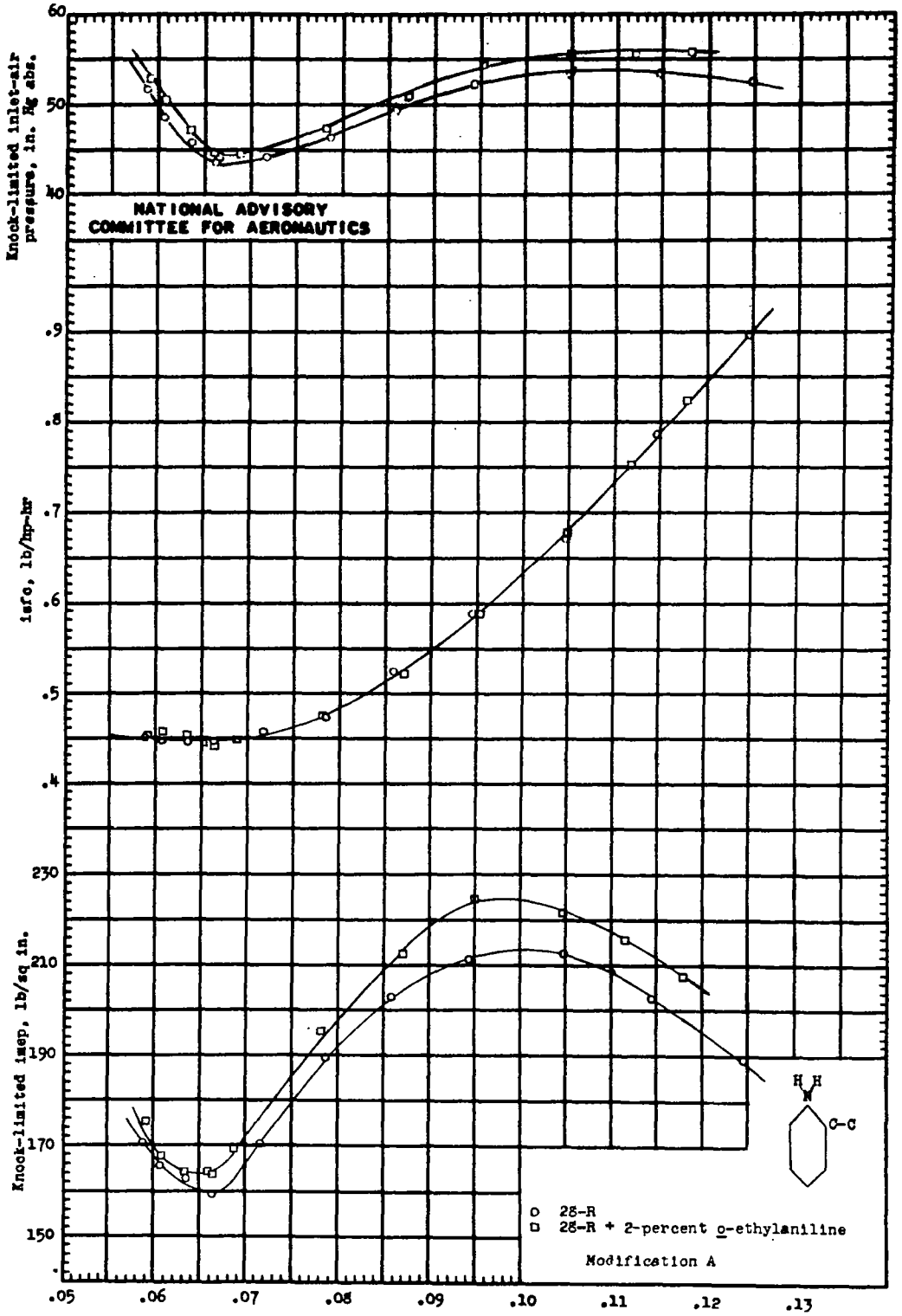
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 4. - Concluded. Effect of addition of 2-percent o-cumidine to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



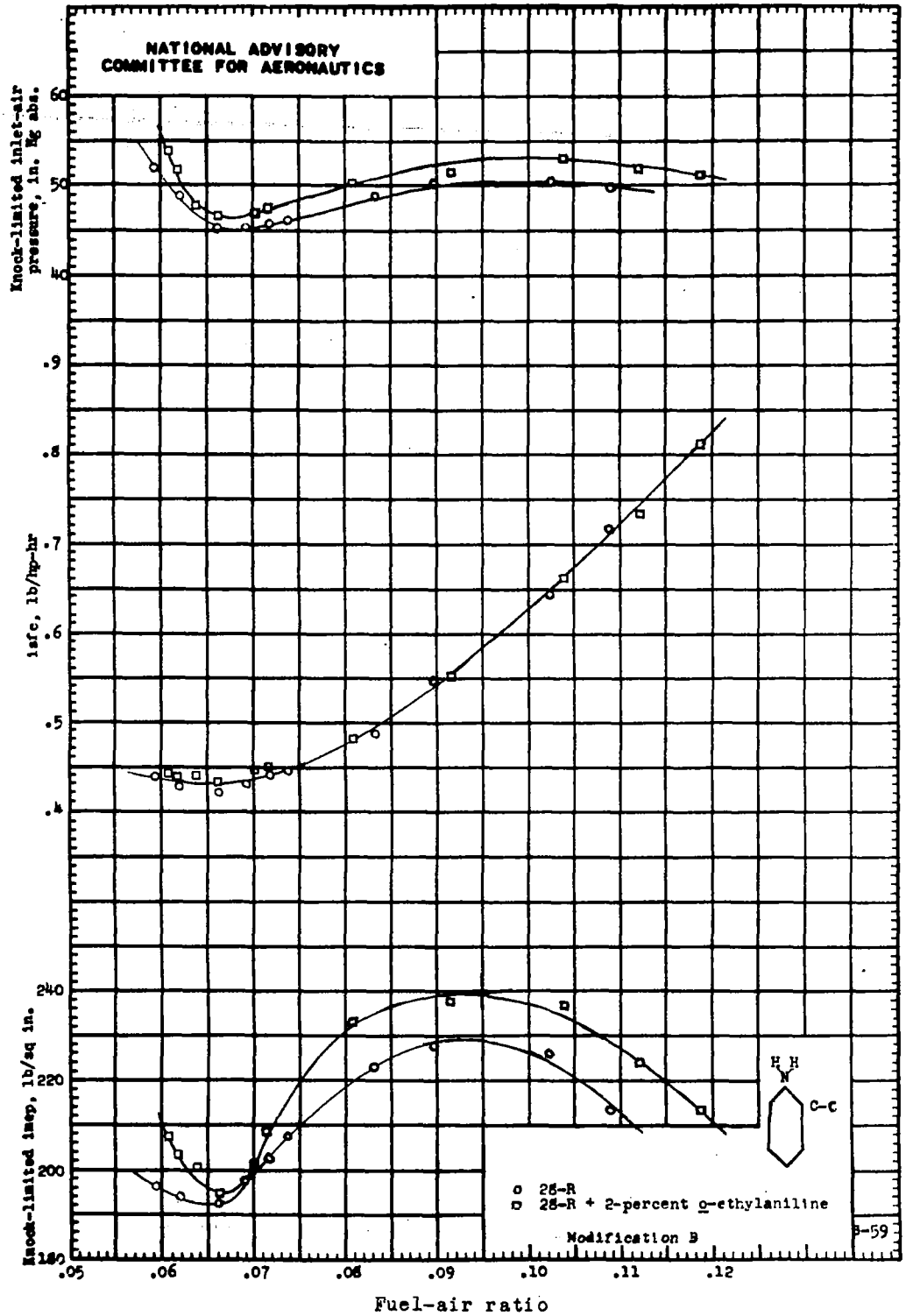
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 5. - Effect of addition of 2-percent o-ethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



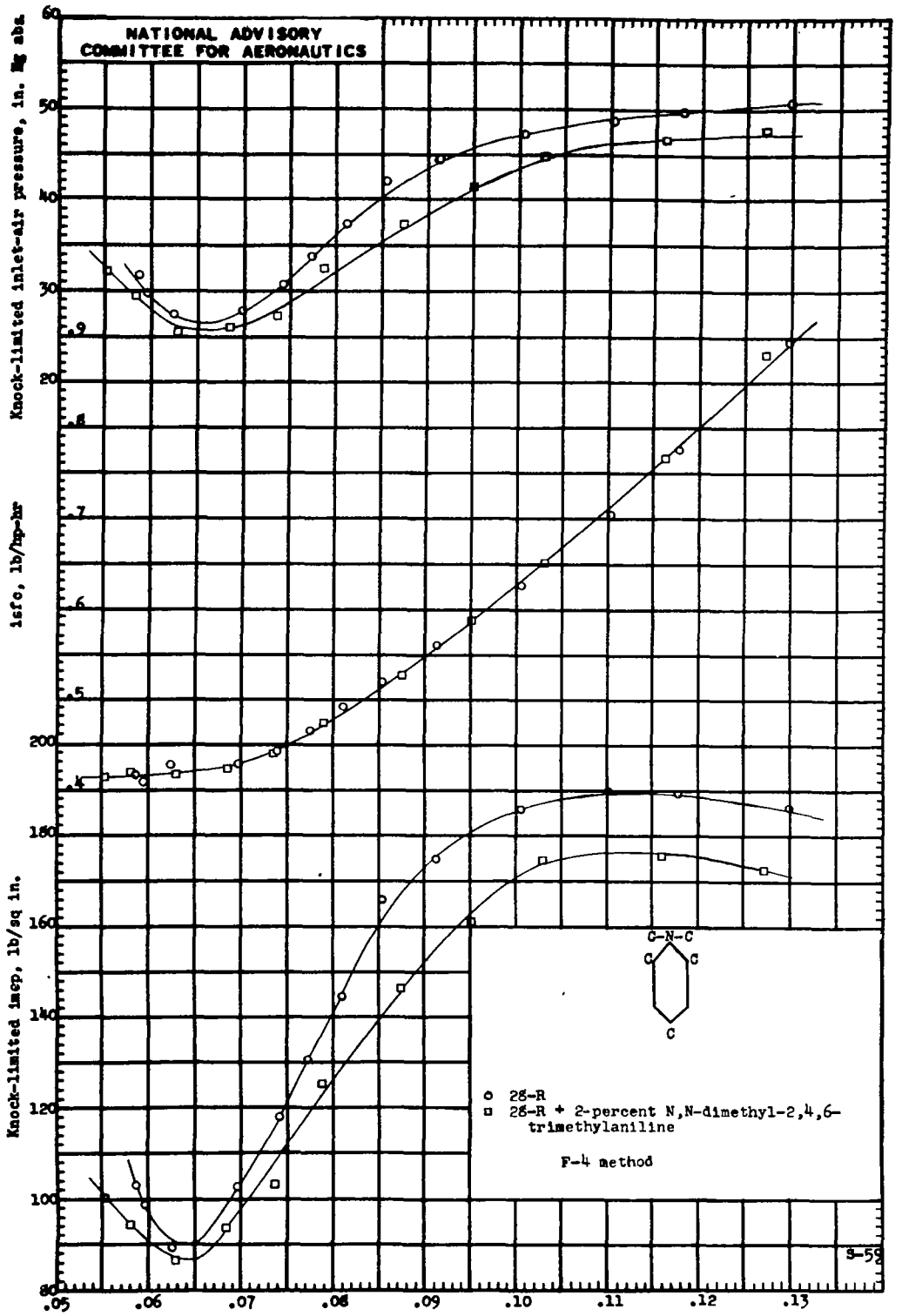
(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 5. - Continued. Effect of addition of 2-percent o-ethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



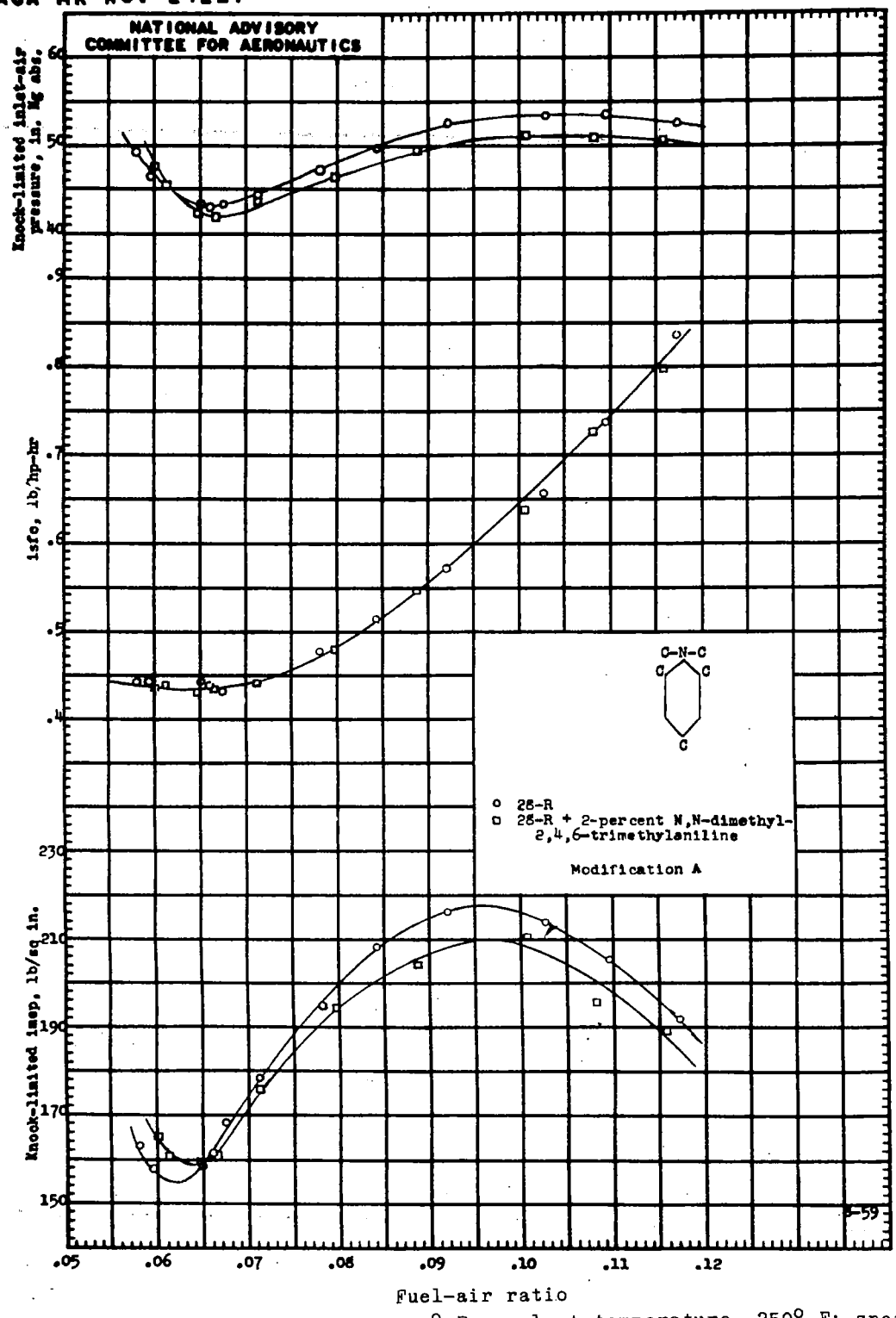
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 5. - Concluded. Effect of addition of 2-percent o-ethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



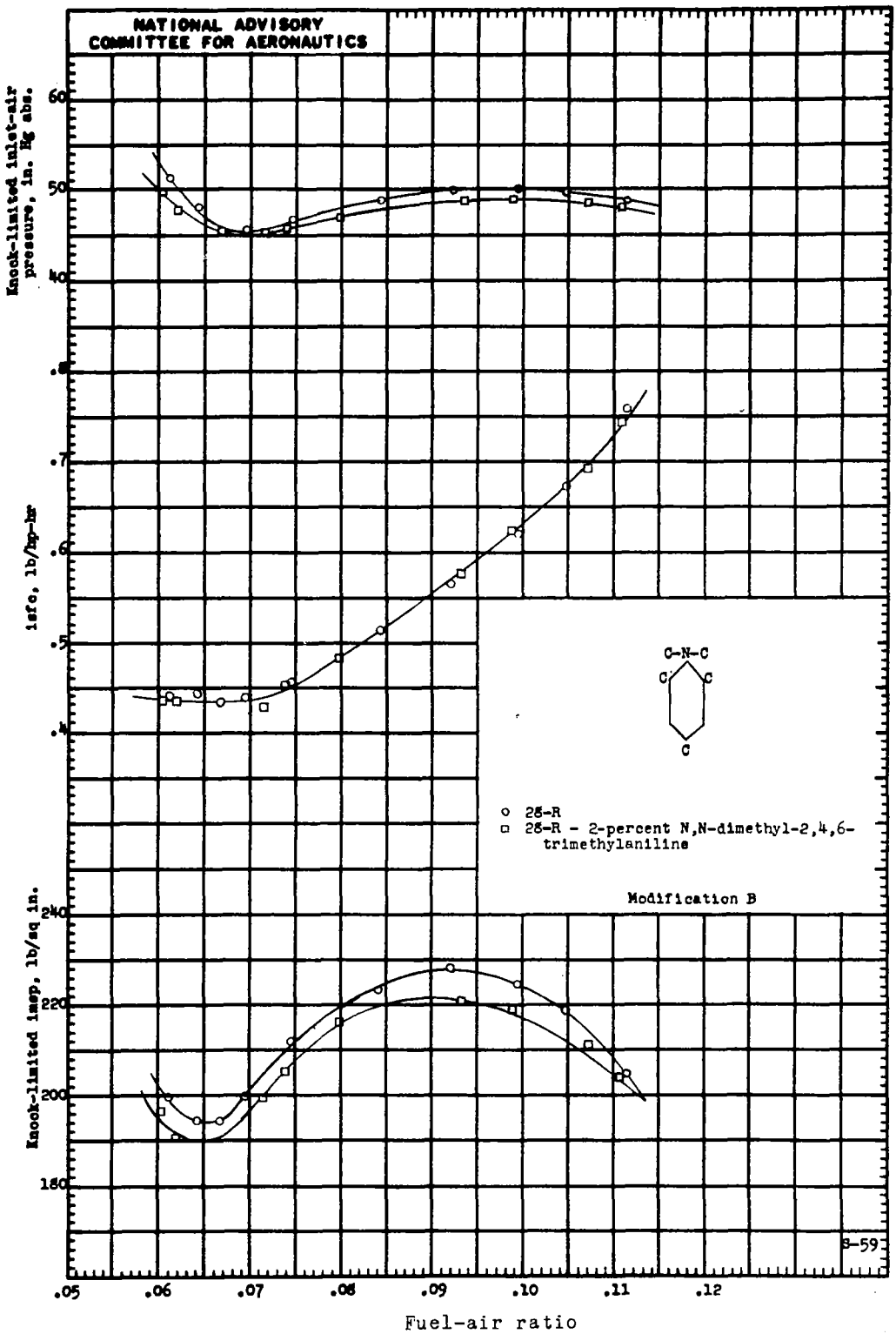
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 6. - Effect of addition of 2-percent N, N-dimethyl-2,4,6-trimethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



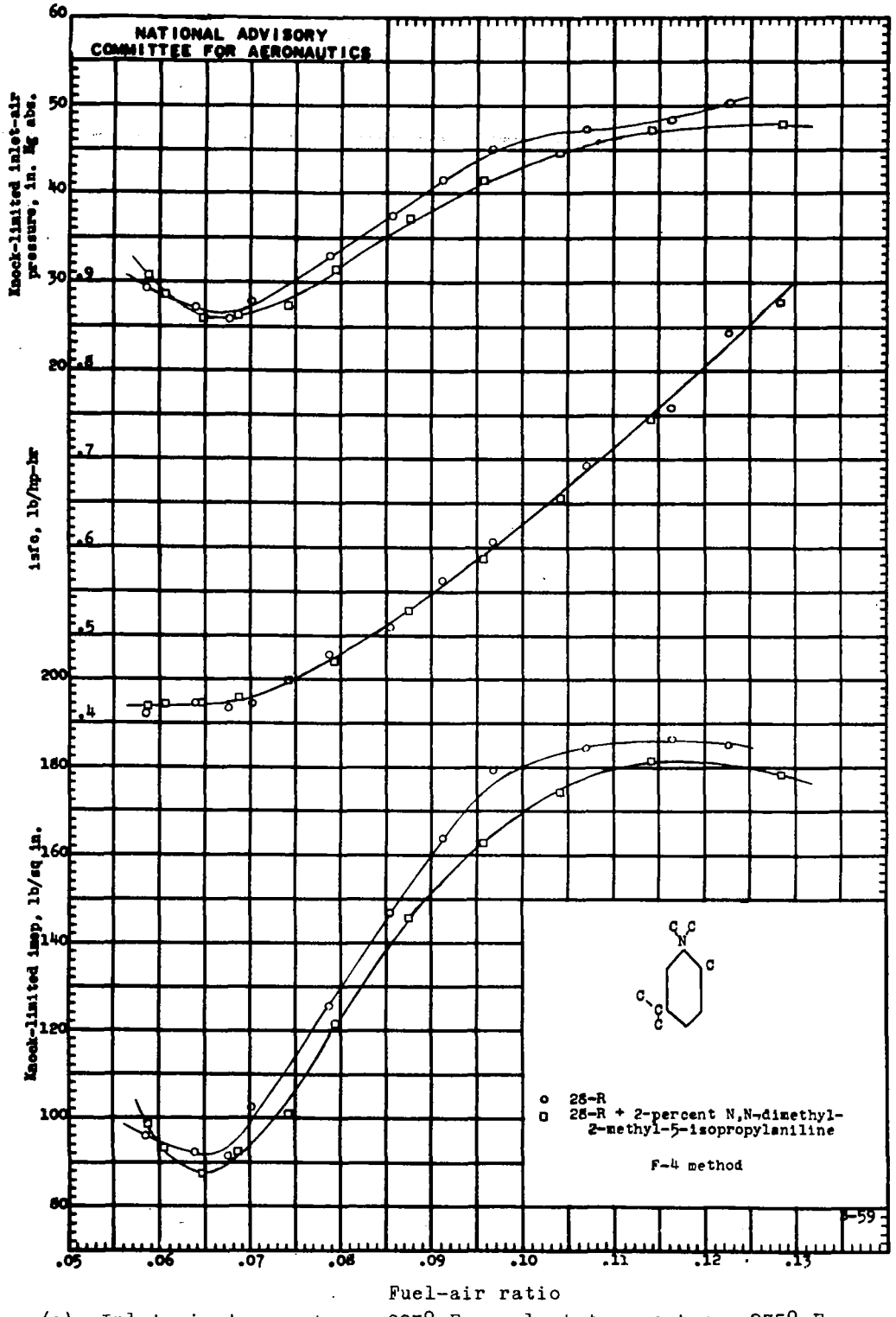
(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 6. - Continued. Effect of addition of 2-percent N, N-dimethyl-2,4,6-trimethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



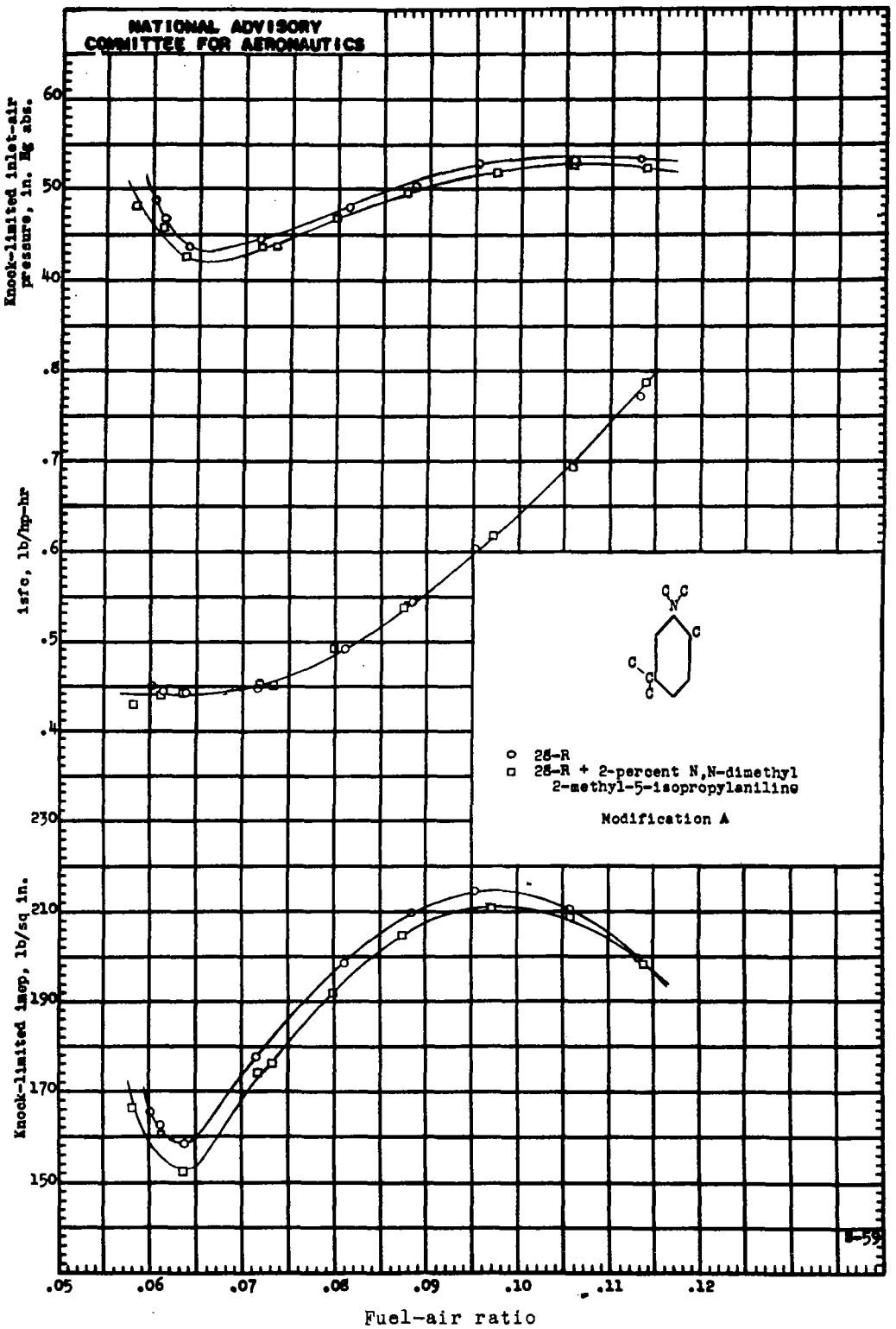
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 6. - Concluded. Effect of addition of 2-percent N, N-dimethyl-2,4,6-trimethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



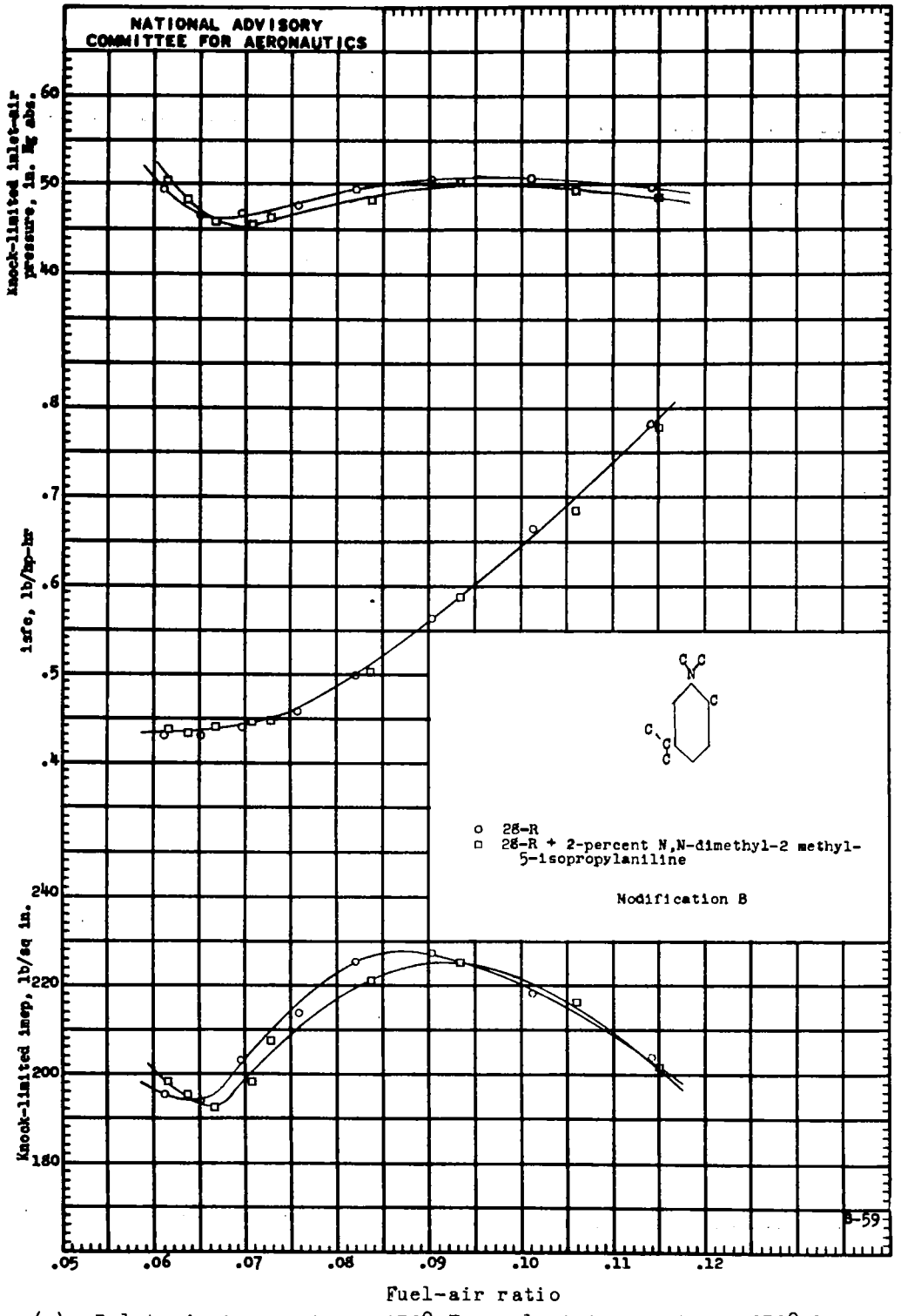
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 7. - Effect of addition of 2-percent N, N-dimethyl-2-methyl-5-isopropylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



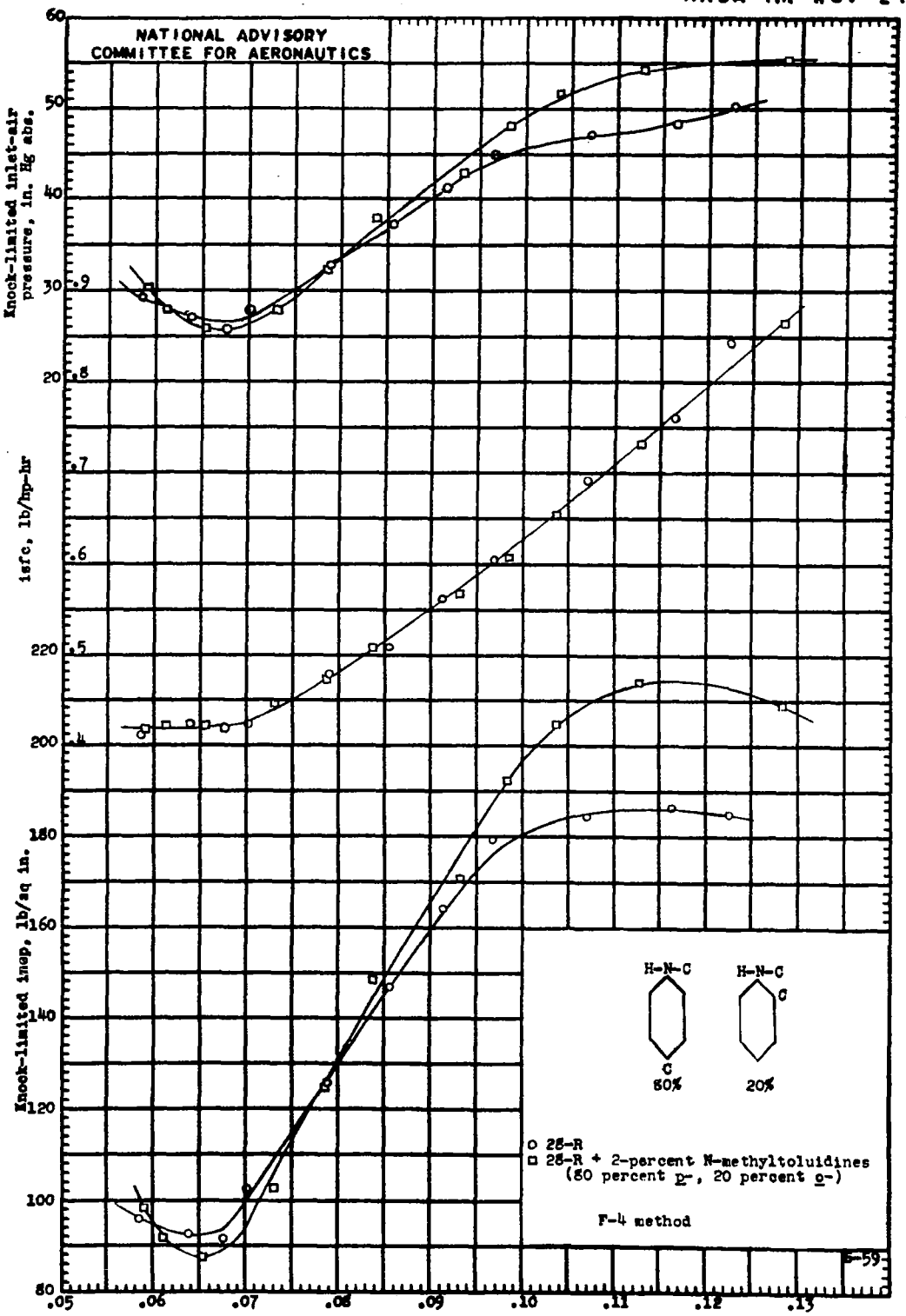
(b) Inlet-air temperature, 250° F; coolant temperature 250° F; spark advance, 30° B.T.C.

Figure 7. - Continued. Effect of addition of 2-percent N, N-dimethyl-2-methyl-5-isopropylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



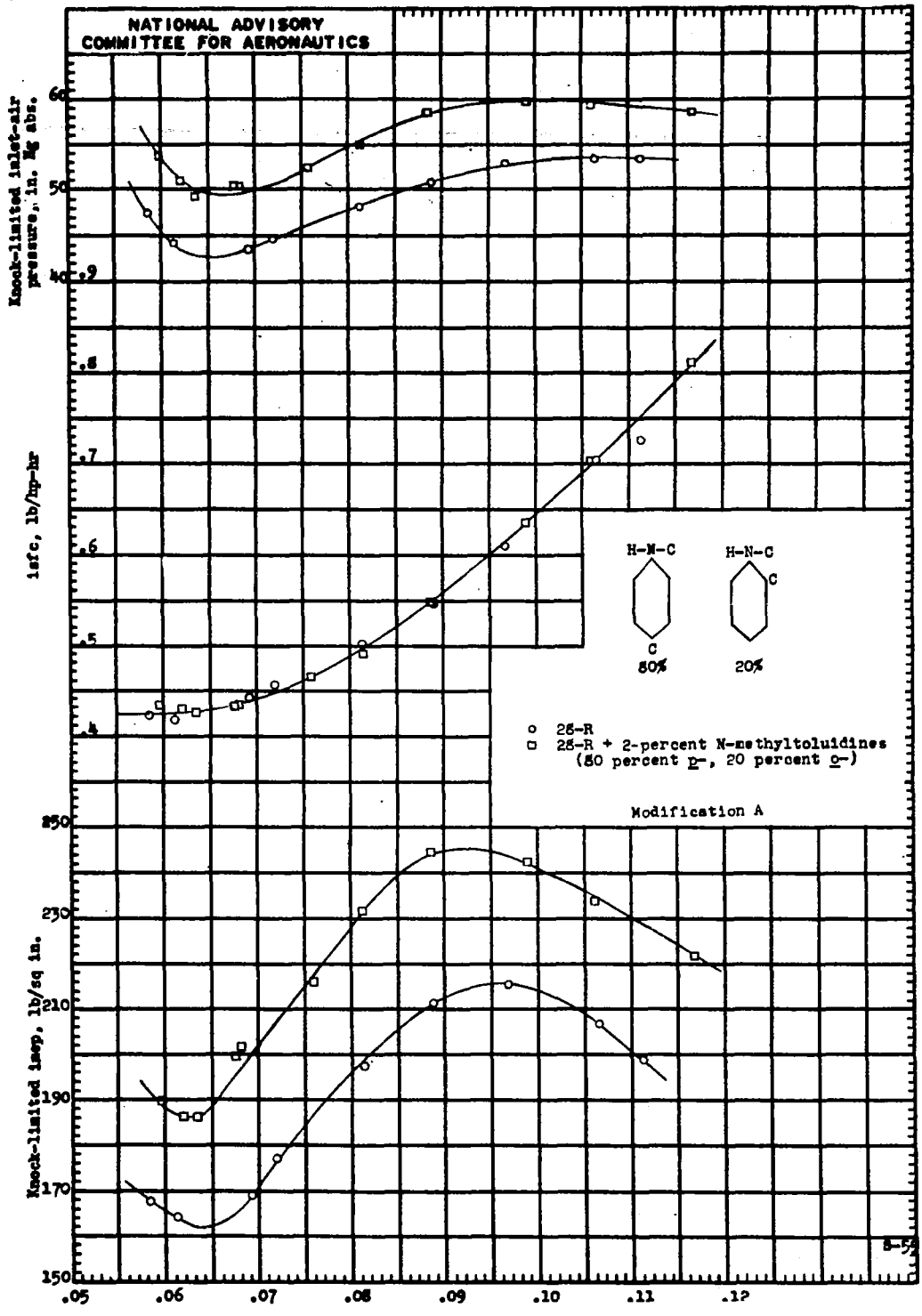
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 7. - Concluded. Effect of addition of 2-percent N, N-dimethyl-2-methyl-5-isopropylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature. 165° F.



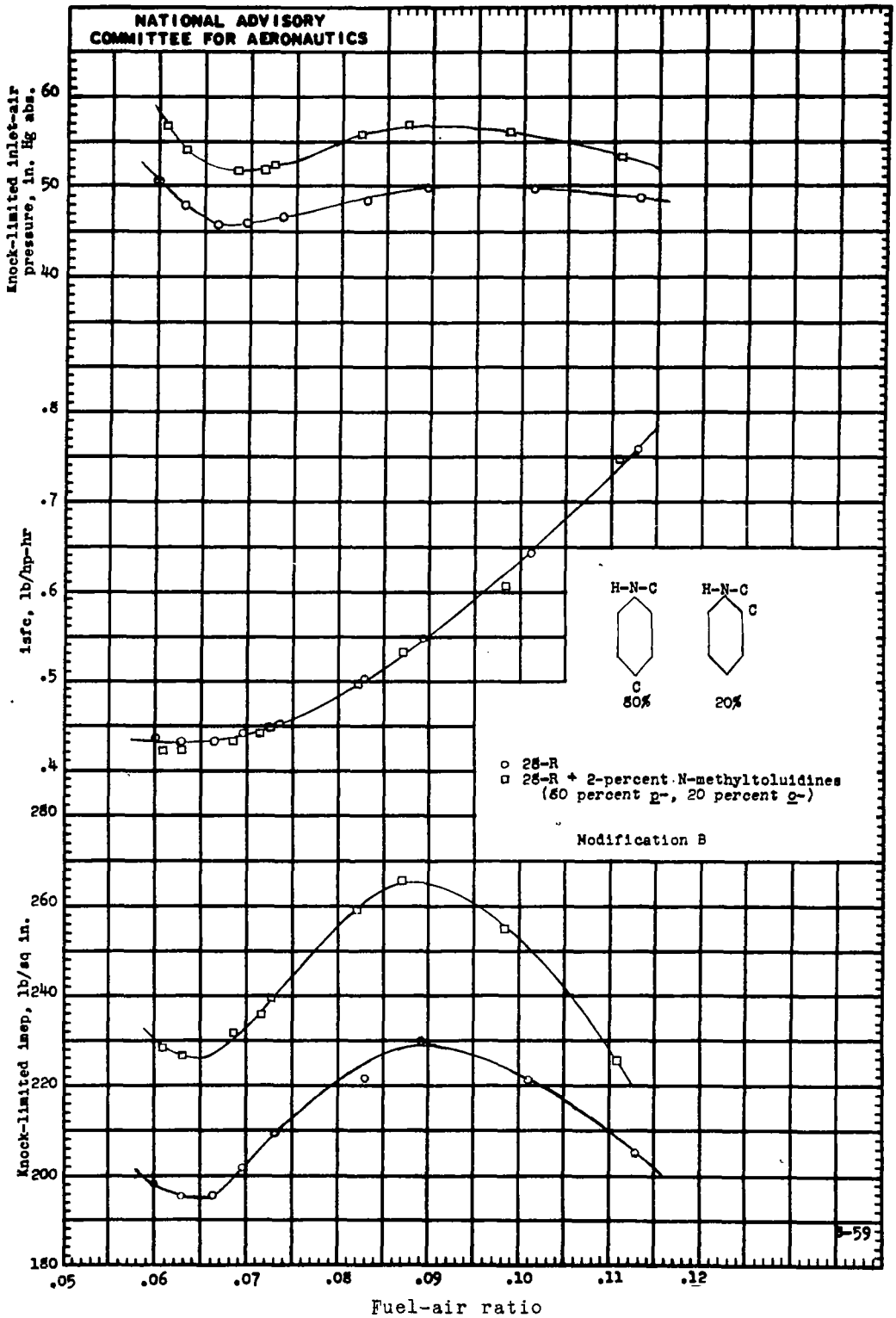
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 8. - Effect of addition of 2-percent N-methyltoluidines (80 percent p-, 20 percent o-) to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



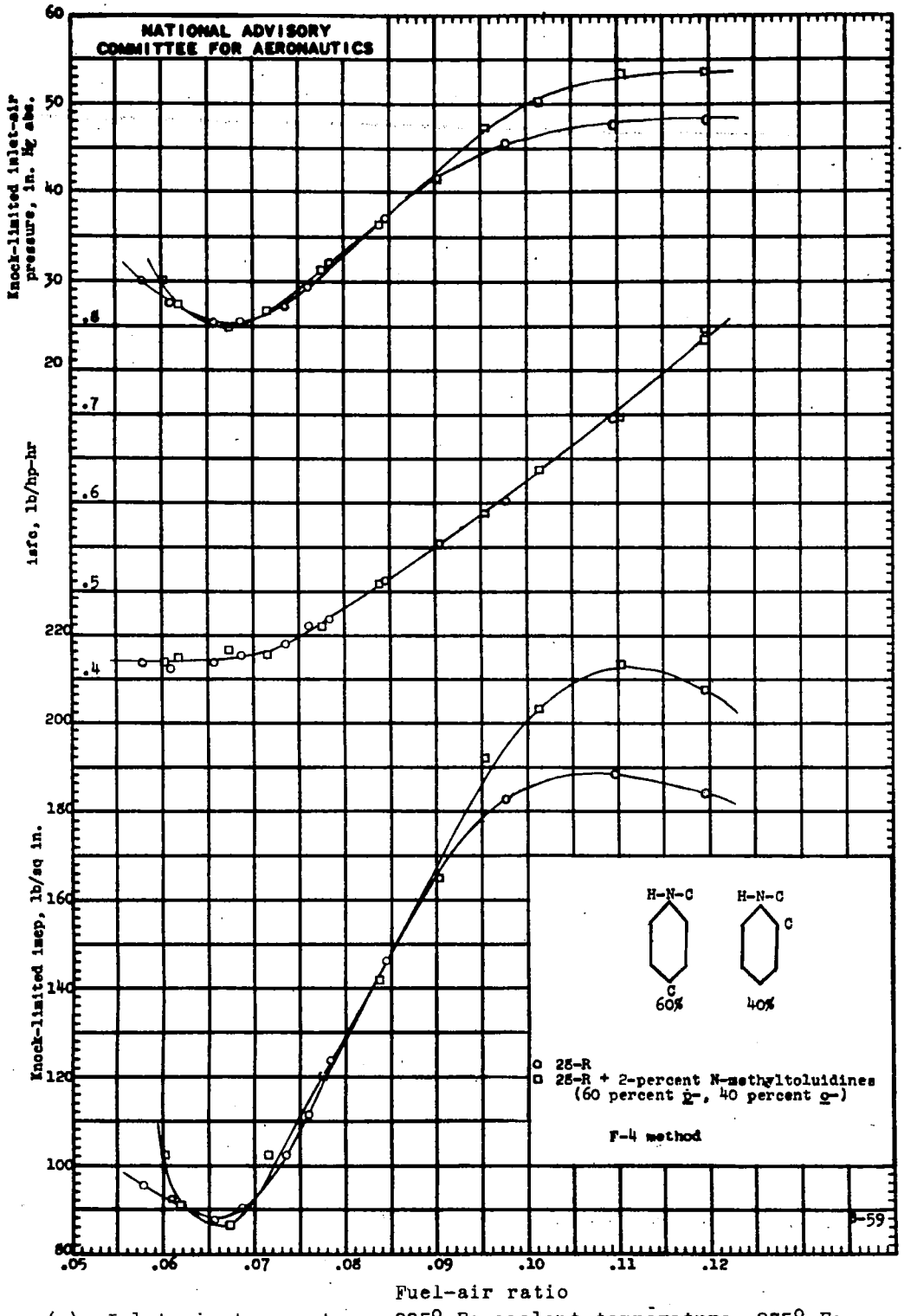
(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 8. - Continued. Effect of addition of 2-percent N-methyltoluidines (80 percent p-, 20 percent o-) to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



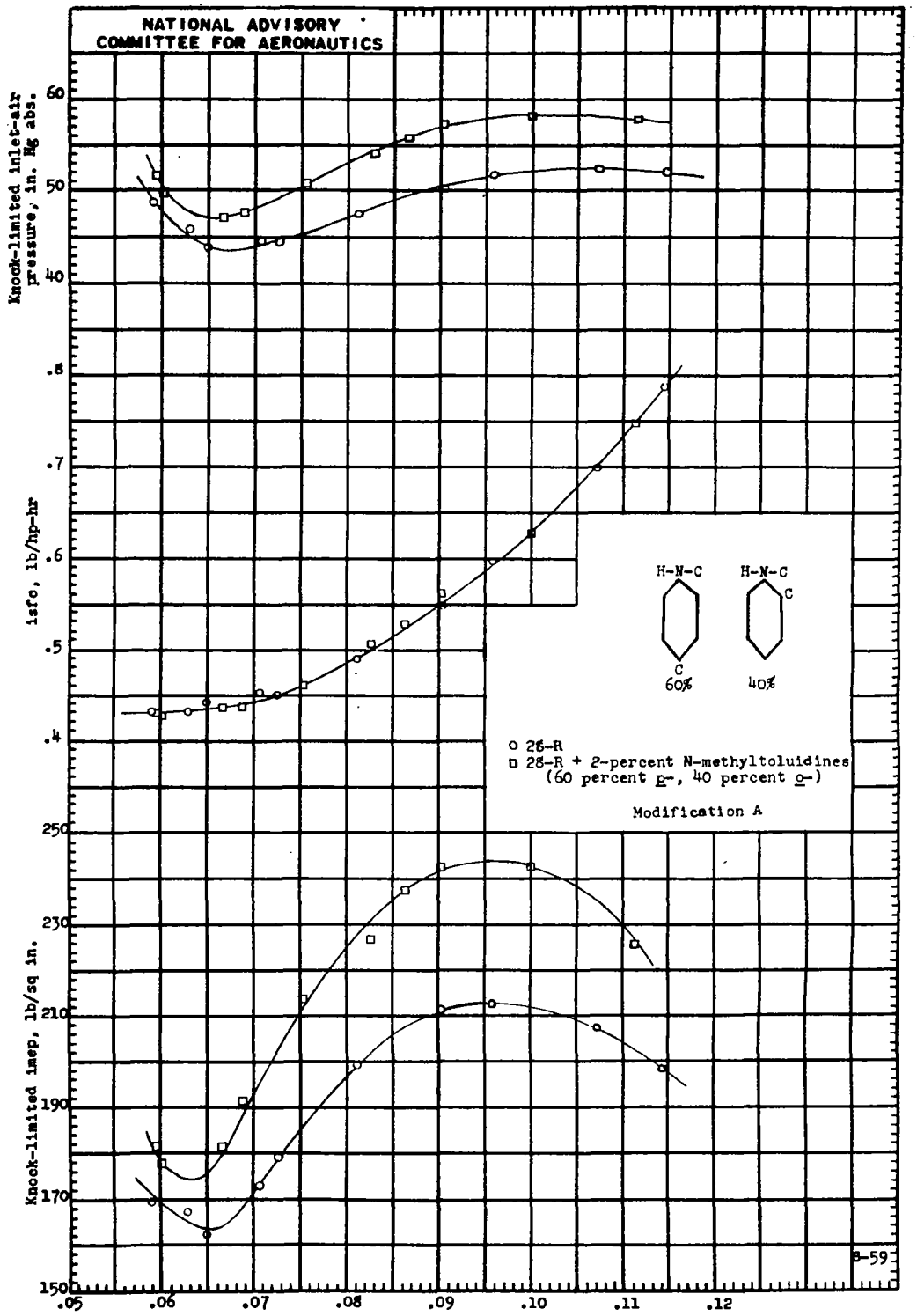
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 8. - Concluded. Effect of addition of 2-percent N-methyltoluidines (80 percent p-, 20 percent o-) to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



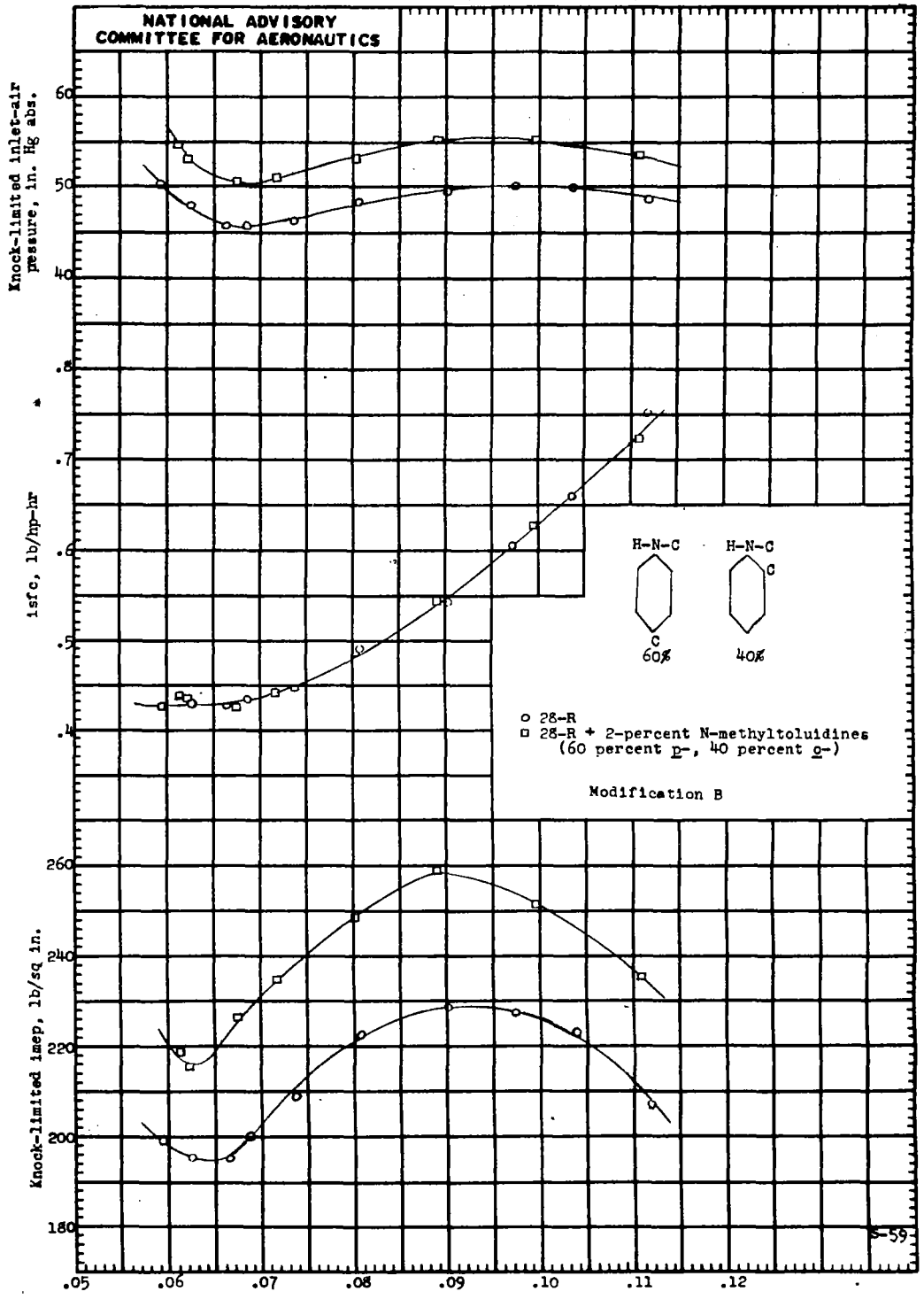
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 9. - Effect of addition of 2-percent N-methyltoluidines (60 percent p-, 40 percent o-) to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



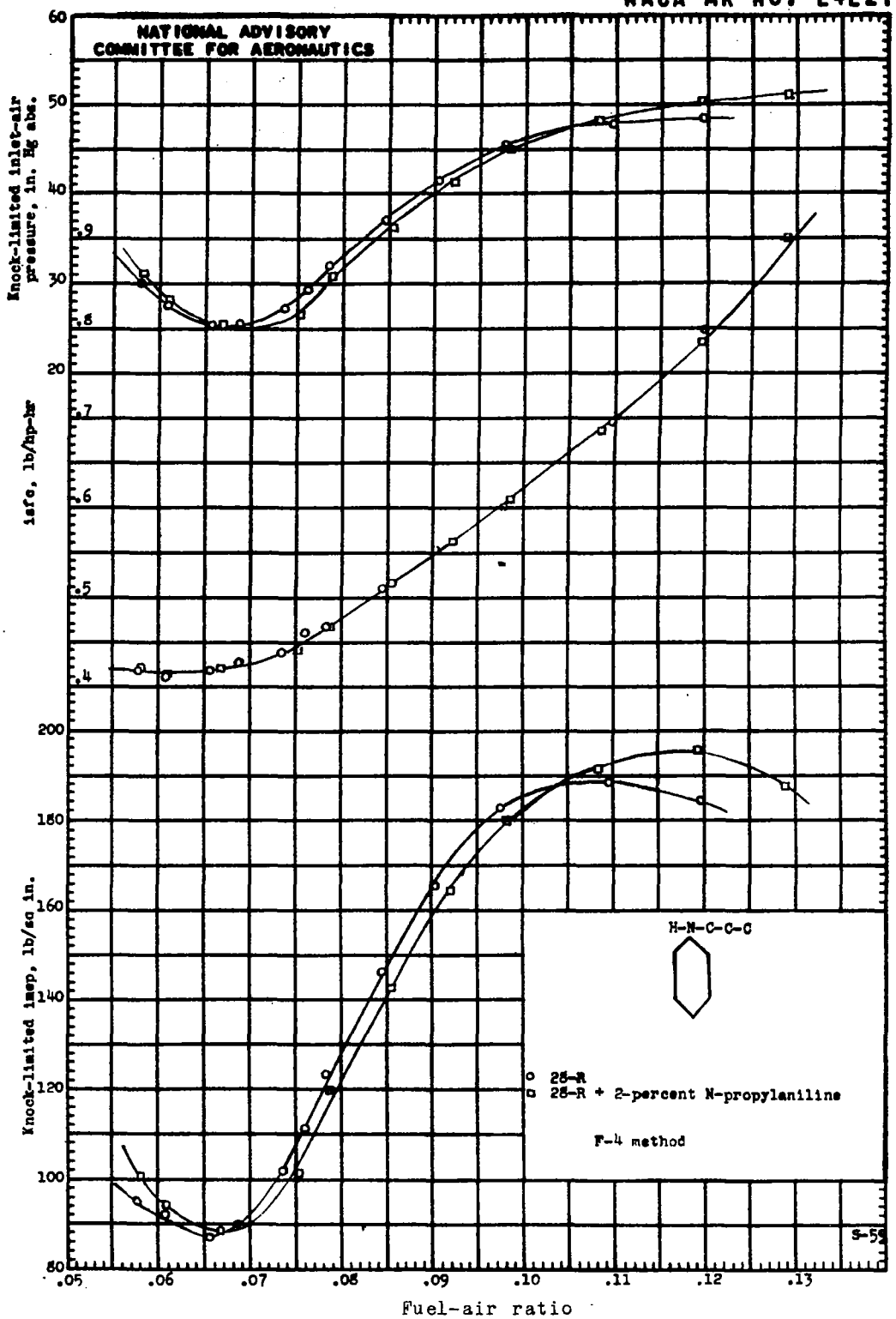
(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 9. - Continued. Effect of addition of 2-percent N-methyltoluidines (60 percent p-, 40 percent o-) to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



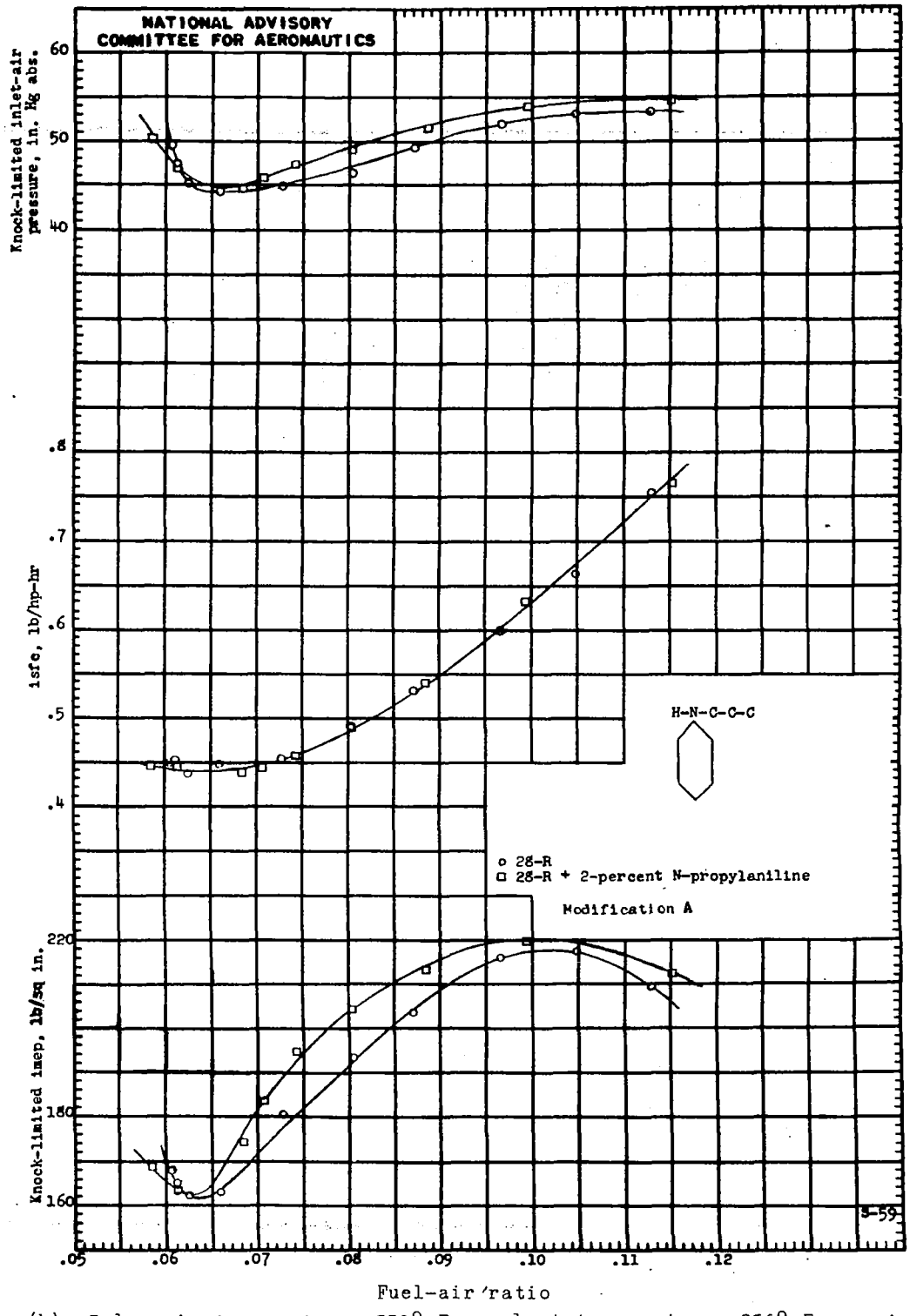
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 9. - Concluded. Effect of addition of 2-percent N-methyltoluidines (60 percent p-, 40 percent o-) to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



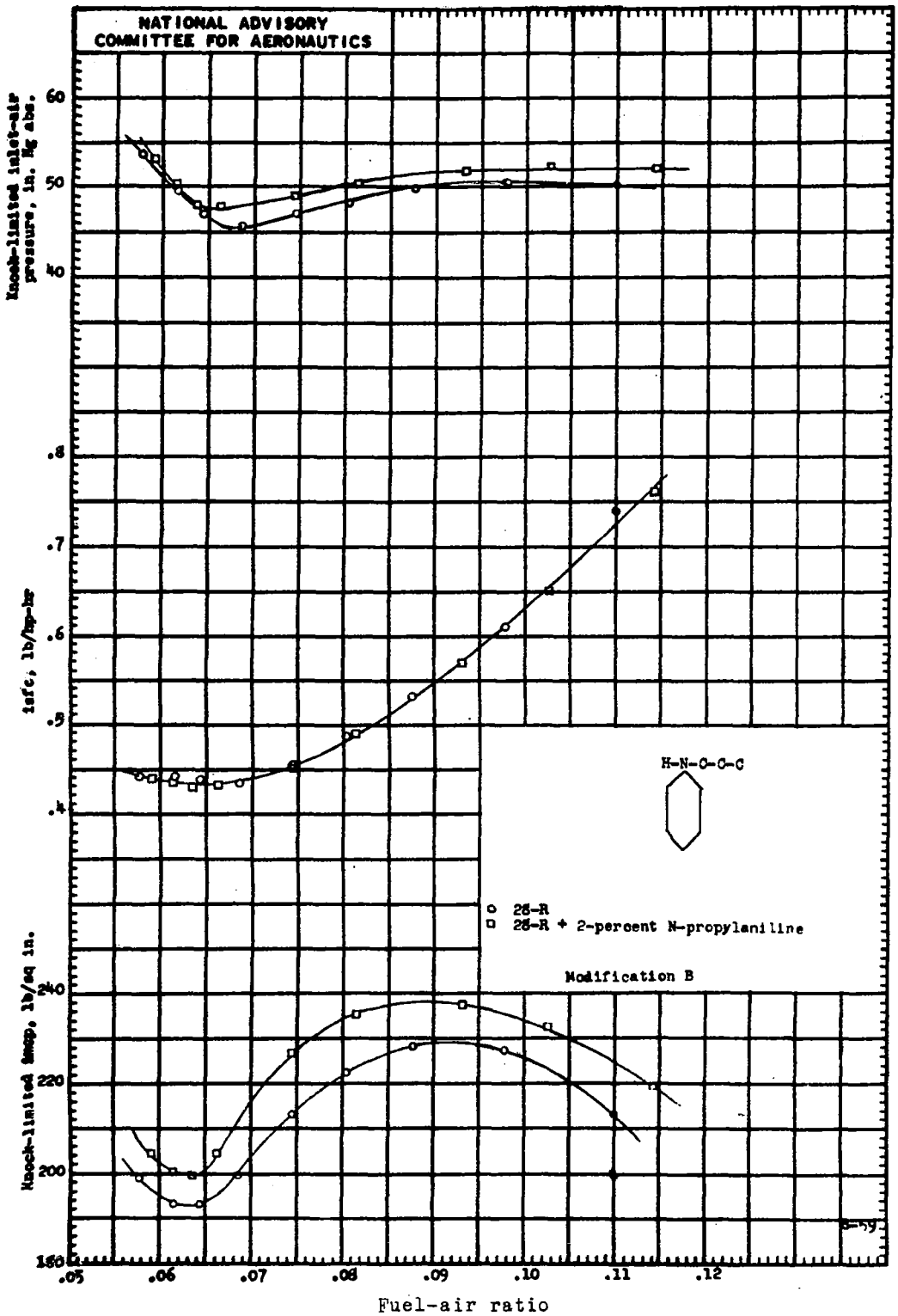
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 10. - Effect of addition of 2-percent N-propylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



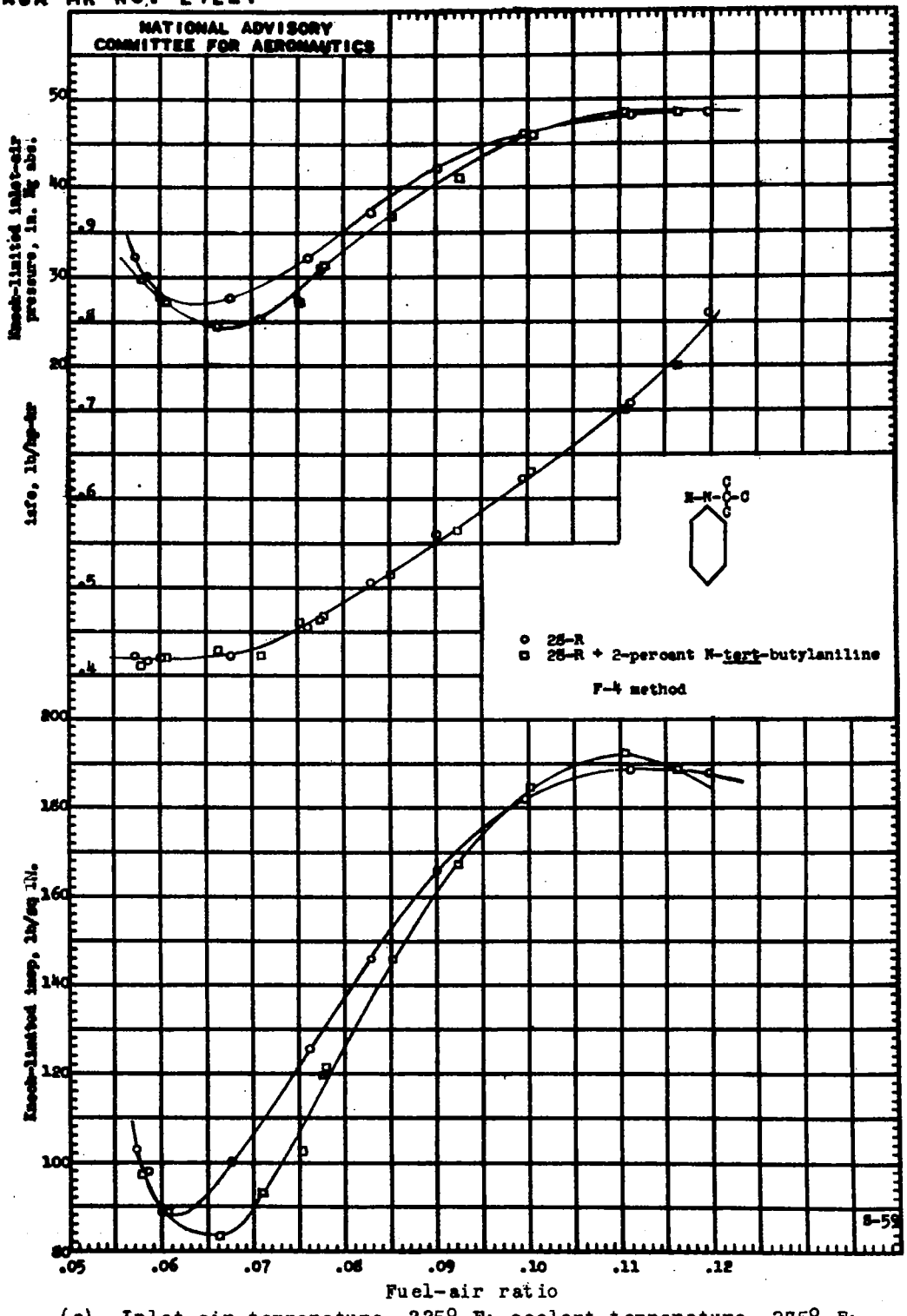
(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 10. - Continued. Effect of addition of 2-percent N-propylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



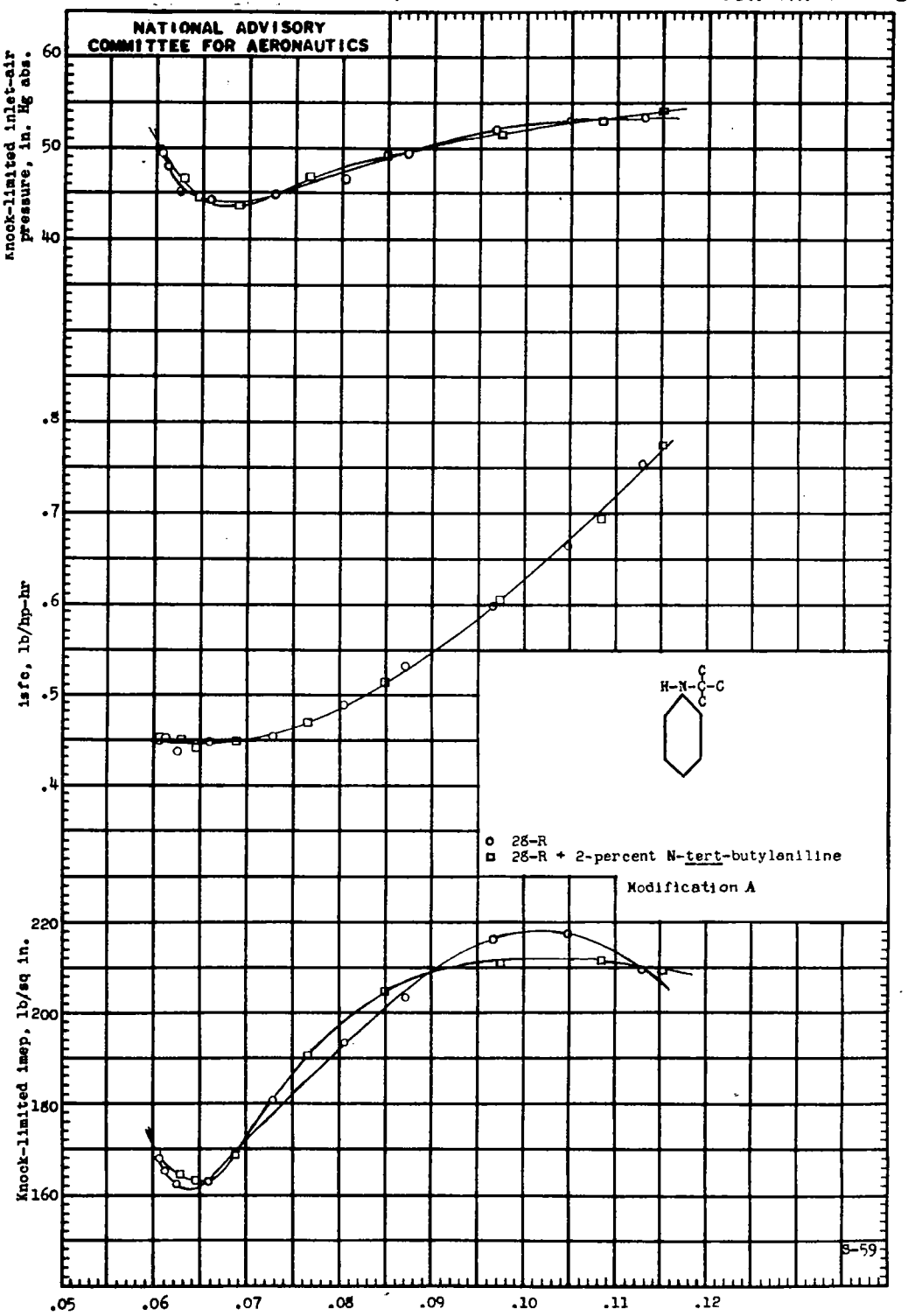
(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 10. - Concluded. Effect of addition of 2-percent N-propylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



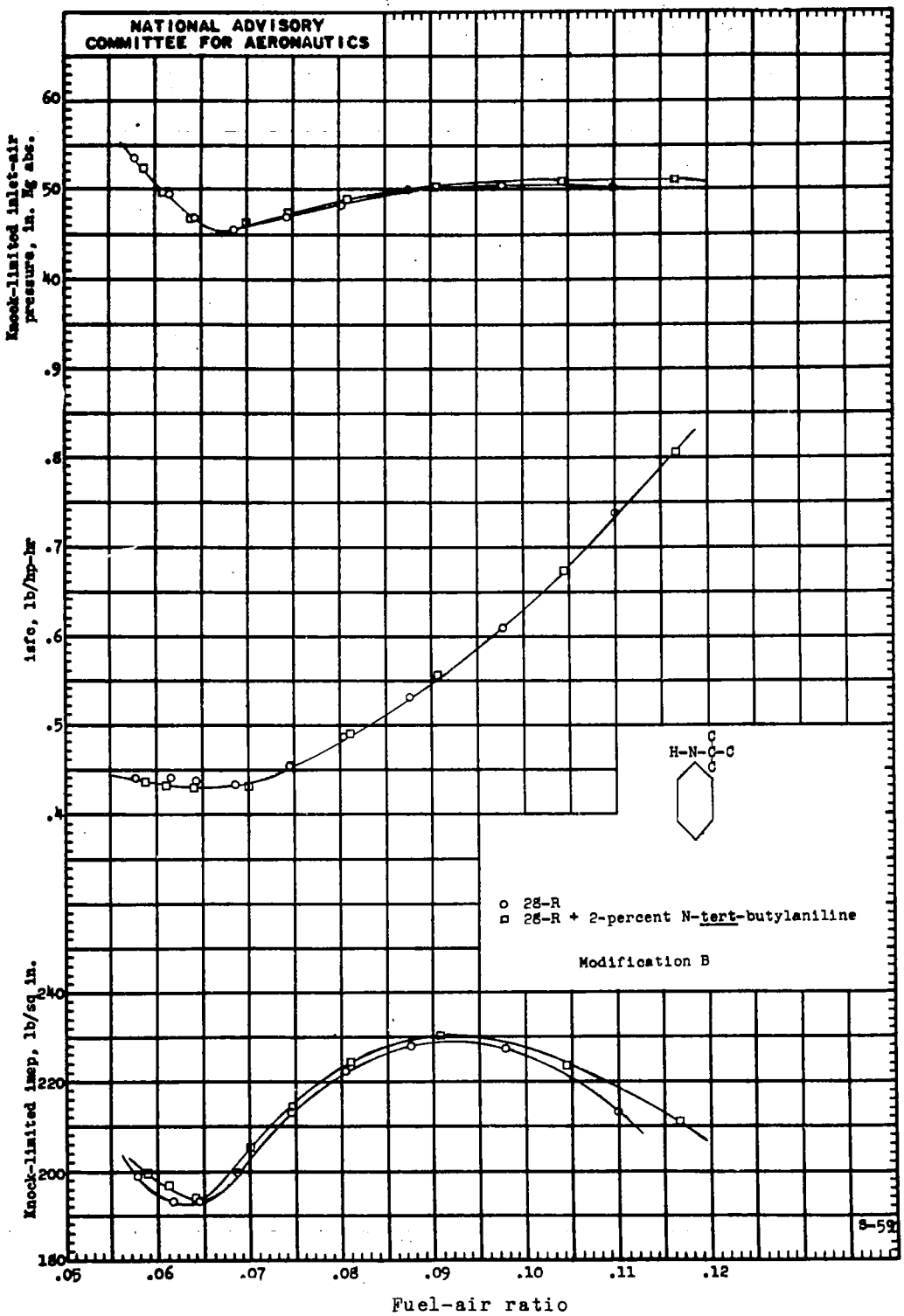
(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 11. - Effect of addition of 2-percent N-tert-butylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



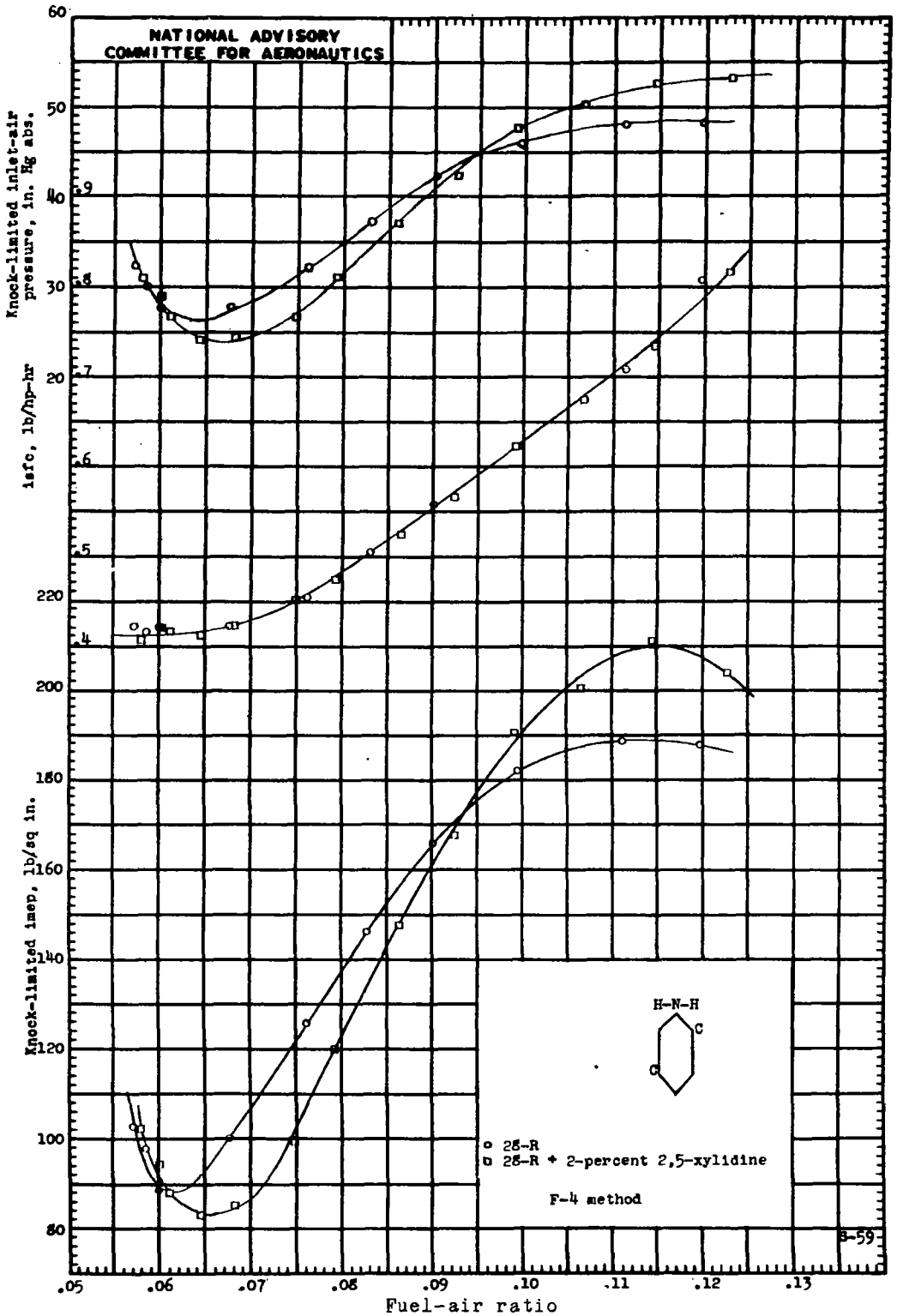
(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 11. - Continued. Effect of addition of 2-percent N-tert-butylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 11. - Concluded. Effect of addition of 2-percent N-tert-butylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

Figure 12. - Effect of addition of 2-percent 2,5-xylidine to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.